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PB-276 620

# Comparison of Wet Chemical and Instrumental Methods for Measuring Airborne Sulfate

California State Dept of Health, Berkeley

Prepared for

Environmental Sciences Research Lab, Research Triangle Park, N C

Nov 77

EPA

PB 276 620

United States
Environmental Protection
Agency

Office of
Research and
Development

Environmental Sciences
Research Laboratory
Research Triangle Park NC 27711

EPA-600/7-77-128
November 1977

# COMPARISON OF WET CHEMICAL AND INSTRUMENTAL METHODS FOR MEASURING AIRBORNE SULFATE
## Final Report

Interagency
Energy-Environment
Research and Development
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## TECHNICAL REPORT DATA

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| | | |
|---|---|---|
| 1. REPORT NO.<br>EPA-600/7-77-128 | 2. | 3. RECIPIENT'S ACCESSION NO.<br>PB276620 |
| 4. TITLE AND SUBTITLE<br>COMPARISON OF WET CHEMICAL AND INSTRUMENTAL METHODS FOR MEASURING AIRBORNE SULFATE<br>Final Report | | 5. REPORT DATE<br>November 1977<br>6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S)<br>B. R. Appel, E. L. Kothny, E. M. Hoffer, and J. J. Wesolowski | | 8. PERFORMING ORGANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Air & Industrial Hygiene Laboratory<br>California Department of Health<br>2151 Berkeley Way<br>Berkeley, California 94704 | | 10. PROGRAM ELEMENT NO.<br>EHE 625 EB-08 (FY-76)<br>11. CONTRACT/GRANT NO.<br>68-02-2273 |
| 12. SPONSORING AGENCY NAME AND ADDRESS<br>Environmental Sciences Research Laboratory - RTP, NC<br>Office of Research and Development<br>U. S. Environmental Protection Agency<br>Research Triangle Park, N.C. 27711 | | 13. TYPE OF REPORT AND PERIOD COVERED<br>FINAL<br>14. SPONSORING AGENCY CODE<br>EPA/600/09 |

15. SUPPLEMENTARY NOTES

This contract was partially funded (47%) by EMSL - RTP.

16. ABSTRACT

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The results demonstrated agreement within 16% for determining atmospheric sulfate concentrations by the three wet chemical procedures with all the filter media. XRF results on the "fine" Fluoropore samples agreed within 10% of those obtained by wet chemical procedures on the samples and were, on average and within experimental error, equivalent to results obtained by the MTB method on 8 x 10" glass fiber high volume samples. Small differences in results obtained with different filter media in the present study are more consistent with the effects of analytical interferents rather than artifact sulfate formation as the cause.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| *Air pollution<br>*Particles<br>*Sulfates<br>*Chemical analysis<br>*Comparison<br>*X-ray fluorescence | | 13B<br>07B<br>07D<br>20F |

| | | |
|---|---|---|
| 18. DISTRIBUTION STATEMENT<br>RELEASE TO PUBLIC | 19. SECURITY CLASS *(This Report)*<br>UNCLASSIFIED | 21. NO. OF PAGES<br>180 |
| | 20. SECURITY CLASS *(This page)*<br>UNCLASSIFIED | 22. PRICE<br>A09 - A01 |

EPA Form 2220-1 (9-73)

EPA-600/7-77-128
November 1977

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# ABSTRACT

The methylthymol blue (MTB), modified Brosset and barium chloranilate sulfate methods were evaluated for precision, accuracy, working range, interference effects and degree of agreement with x-ray fluorescence analysis (XRF) using atmospheric particulate samples. The samples used were collected simultaneously with glass fiber, quartz fiber and Fluoropore filters, the latter being in a dichotomous sampler. The sampling design also permitted an evaluation of artifact sulfate formation and other filter media-specific effects. Studies of interference effects were based upon measured concentrations of potential interferents extractable from the particulate matter as well as the filter media. Interferents were evaluated singly, in pairs and quartets seeking evidence of interactions yielding non-additivity of effects.

The results demonstrated agreement within 16% for determining atmospheric sulfate concentrations by the three wet chemical procedures with all the filter media. XRF results on the "fine" Fluoropore samples agreed within 10% of those obtained by wet chemical procedures on the same samples and were, on average and within experimental error, equivalent to results obtained by the MTB method on 8 x 10" glass fiber high volume samples. Small differences in results obtained with different filter media in the present study are more consistent with the effects of analytical interferents rather than artifact sulfate formation as the cause.

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# ACKNOWLEDGMENTS

Other participants in this study included G. Buell and S. Wall, who carried out the modified Brosset and methylthymol blue analyses, respectively; S. Twiss, who supervised data reduction and display; and M. Haik, who supervised sample handling and logistics.

In addition, we wish to acknowledge T. Dzubay of the Environmental Protection Agency, who provided the x-ray fluorescence analyses discussed in this report, and R. Coutant, Battelle Columbus Laboratory, for his data on artifact sulfate formation, and J. Stikeleather, Northrup Services, Inc., for helpful discussions on the Brosset method.

Mrs. Carole Sawicki and Mr. Michael Beard served as Co-Project Officers for this program. Their helpfulness throughout this work has been sincerely appreciated.

## I. INTRODUCTION

In the first year of this two-year study[1], four wet chemical sulfate methods were evaluated and compared to each other and to total sulfur determinations by x-ray fluorescence analysis (XRF). The wet chemical methods studied included:

A. The $BaCl_2$ turbidimetric procedure

B. The methylthymol blue procedure as automated for the Technicon Autoanalyzer II (MTB)

C. The AIHL microchemical procedure

D. A modified Brosset procedure

The specific parameters evaluated included precision, accuracy, agreement between methods, and the effect of a number of potential interferents.

The second year of this study had as its objectives:

A. Evaluation of the working ranges of three wet chemical sulfate methods, including assessment of precision and accuracy.

B. Evaluation of the influence of interferents singly, in pairs, and quartets on determination of sulfate by the three methods.

C. Analysis of approximately 100 St. Louis air samples for sulfate by the three methods with and without correction for the observed influence of interferents.

D. Intercomparison of wet chemical and x-ray fluorescence (XRF) total sulfur analyses with ambient air samples.

The wet chemical methods were the automated methylthymol blue (MTB) procedure, a manual barium chloranilate method (BC) and a semi-automated modified Brosset (Brosset) procedure. The latter was another version from that evaluated in the first year of the study, differing in the solvent and the use of semi-automated equipment.

Since the atmospheric samples were collected with side-by-side sampling of both glass fiber and more inert filter media, an evaluation of the extent of artifact sulfate formation has been made for these samples.

This report concentrates on the efforts of the second year. The first year's study is summarized in EPA Report No. 600/2-76-059.

## II. SUMMARY AND CONCLUSIONS

The working ranges of the automated methylthymol blue (MTB), semiautomated, modified Brosset (Brosset) and manual barium chloranilate (BC) methods were evaluated using as criteria constancy of variance and accuracy with standards and atmospheric samples. With atmospheric samples, accuracy was assessed relative to the sulfate determined for analyses at the mid-range of each method. While data reduction employed primarily linear regression with all methods, the evaluation of the MTB method compared linear regression and a third order polynomial fit to the working curve. Using linear regression, the working range of the MTB method was established to be 7-75 μg/ml. Using a third order fit, the working range could be extended down to ca. 4 μg/ml. The working range for the Brosset method was shown to be 3-13 μg/ml.

Following the criteria stated, the working range for the BC method would be from 10 to 40 μg/ml since the variance increased markedly at higher levels. However, if a variance corresponding to a coefficient of variation of 6% is acceptable, the working range can be considered 10-50 μg/ml.

Using EPA audit samples (glass fiber filter strips spiked with known quantities of sulfate), the accuracy of the MTB, Brosset and BC methods was, on average, 93%, 104% and 98%, respectively.

About one hundred atmospheric samples were collected by EPA personnel in St. Louis with side-by-side sampling using a hi-vol (8 x 10" glass fiber), two low-volume 126 mm filter samplers using glass fiber and quartz fiber, and a dichotomous sampler with 37 mm Fluoropore filters. These samples permitted evaluation of precision, agreement between methods, comparison with XRF for total sulfur, determination of analytical interferents present in aqueous extracts of the atmospheric samples, and an evaluation of filter media effects in sulfate collection.

With atmospheric samples, the precision of the three methods differed significantly. The MTB method exhibited a coefficient of variation of 1-2% compared to 5-9% for the modified Brosset and BC methods. Average results by the three wet chemical methods differed by up to 16% with the degree of agreement varying with filter type. Apparent sulfate concentrations with the glass fiber hi-vol and quartz samples agreed within 3%, while Fluoropore and glass fiber low-vol showed greater differences relative to the hi-vol samples. Fluoropore filters were analyzed by XRF in addition to the three wet chemical methods. The XRF results agreed, on average, within 10% with those obtained by the MTB and modified Brosset methods.

The regression equations relating results between methods are as follows:

Brosset = 0.93 [MTB]-0.61 r = 0.75 (126 mm glass fiber)
Brosset = 1.03 [MTB]-0.27 r = 0.997 (126 mm quartz fiber)
Brosset = 0.97 [MTB]-0.49 r = 0.996 (Fluoropore filters)
(3rd order regression for MTB method)
BC = 0.92 [MTB]+0.89 r = 0.999 (Hi-vol (glass))
BC = 0.95 [MTB]-1.49 r = 0.86 (Fluoropore)
BC = 0.93 [MTB]-1.56 r = 0.99 (126 mm glass fiber)
BC = 0.91 [MTB]+0.68 r = 0.98 (126 mm quartz fiber)

XRF = 0.71 [MTB]+3.37 r = 0.98 (Fluoropore)
(3rd order regression for MTB method)

XRF = 0.73 [Brosset]+3.74 r = 0.98 (Fluoropore)

The average agreement between methods, expressed as a ratio of means, for the Fluoropore samples was as follows:

Brosset/MTB = 0.93

BC/MTB = 0.87

XRF/MTB = 0.91

Aqueous extracts from atmospheric samples were analyzed for a number of potential interferents in sulfate determination including silicate, phosphate, chloride, turbidity (as colloidal clay) and "yellowness" (as p-benzoquinone). In addition, filter sections were analyzed for sulfite.

Based on the maximum observed concentrations, a study of interference effects was designed including evaluations with interferents singly, in pairs and quartets. The multiple interferents were studied seeking evidence of possible non-additivity.

The Brosset method proved to be sensitive to the fewest interferents and the MTB method, to the greatest number. The MTB method was subject to significant (i.e. > 5%) positive interference by silicate, phosphate and colloidal clay, while colloidal clay and p-benzoquinone gave significant positive and negative interference, respectively, with the modified Brosset technique. The BC method was subject to positive interference by phosphate, chloride, clay and p-benzoquinone. Studies of interferents in quartets revealed evidence of some interaction between interferents with the MTB and

BC methods; observed interferences were about half of the sum of the effects observed singly.

Observed interferents in atmospheric samples resulted from both the filter media and the particulate matter. Based on measured interferent concentrations in atmospheric samples and the interference effects study, an estimate of the maximum likely error in sulfate concentration has been made for each filter type and analytical method. The 126 mm glass fiber filters appear to cause the greatest interference with a maximal error of 1.6 $\mu g/m^3$ by the MTB method. The error for the glass fiber hi-vol filter is only 0.5 $\mu g/m^3$ primarily because of the larger air volumes sampled.

An estimate of artifact sulfate formation was made based on reported $SO_2$ concentrations for 5 of the particulate sampling days. Using these data and the results of R. Coutant of the Battelle Laboratory (Columbus), artifact sulfate levels of ca. 1 $\mu g/m^3$ are estimated for the 24-hour 8 x 10" glass fiber filters used in the current program. However, the conductimetric $SO_2$ method used, is known to be subject to substantial positive interferences making the estimate of artifact sulfate probably too high.

Results on the different filter media depended on the analytical method used. With the MTB method, the 126 mm glass fiber results were 10-15% higher than those on the quartz, Fluoropore and 8 x 10" glass fiber filters, while by the Brosset method, the 126 mm glass and quartz results agree well but the Fluoropore results (on < 2 μm particles) were 10%

lower. As discussed in Section VIII, these findings are consistent with the effects of analytical interferents rather than artifact sulfate formation.

Based upon the present study, the Brosset technique is a rapid and reliable procedure for samples in the 3-13 μg/ml sulfate range. Similarly, the MTB method proved to be a rapid and reliable method for samples in the 7-75 μg/ml range. The barium chloranilate procedure, while providing good accuracy with standards, exhibited relatively poor precision and cannot be recommended for use without further modification.

The key conclusions from this study are the following:

1. The automated methylthymol blue, Brosset and barium chloranilate procedures yield results agreeing within 16% when applied to ambient air samples collected on three different filter media.
2. X-ray fluorescence analysis of samples collected on Fluoropore filters yields mean sulfur concentrations (as sulfate) within 10% of those obtained by the wet chemical procedures. The XRF results on Fluoropore and those by MTB analysis on 8 x 10" glass fiber hi-volume samples were, on average, equivalent.
3. Analytical interference with the MTB method can yield significantly higher sulfate results with glass fiber compared to other filter samples.
4. The interferences shown in the wet chemical sulfate methods point out the need to make appropriate corrections.

## III. EVALUATION OF THE AUTOMATED METHYLTHYMOL BLUE (MTB) METHOD

### A. Analytical Protocol

The MTB method was set up in the Fall of 1974, and operated following the protocol given by Technicon for the Autoanalyzer II (AA II) as modified by AIHL[1]. The technique used differs somewhat from that described in the EMSL/RTP procedure for the Auto Technicon II. These differences are enumerated in detail in Appendix A. The principal differences relate to the use of a linearizer and the technique for data reduction. The EMSL/RTP procedure for the AA II requires a linearizer. Since such equipment was not available, AIHL analyses used linear regression for fitting the working curve, analyzed samples in the linear region of the working curve and compared linear and non-linear curve fitting techniques, including a power function and a third order polynomial fit.

### B. Working Range

The definition of the "working range" as provided by EPA is the region of constant variance. Our evaluation employed both this concept, using standard solutions and particulate extracts, and an evaluation of accuracy as a function of concentration. The latter is relevant because the MTB (and other) working curves are non-linear at their extremes.

To evaluate accuracy with an atmospheric sample, a hi-vol sample extract was analyzed after dilution to the optimal range of the MTB method. The sulfate concentration calculated for the undiluted solution was considered "correct". By analyzing aliquots of this solution diluted to varying degrees, the accuracy of the method was evaluated relative to the optimal value obtained with the method. We henceforth refer to this as "relative accuracy". A detailed protocol is included in Appendix B.

The relative accuracy calculated for the MTB method with sulfate concentrations at the extremes of the working curve is expected to depend on the regression equation employed for fitting the working curve. Therefore, in addition to the work conducted under the protocol in Appendix B (which used linear regression), linear regression was compared to other techniques using both standards and a hi-vol extract.

Figure 1 plots the working curve between 4 and 75 μg/ml. The error bars are ± 2 σ. The line shown is the best linear least squares fit between 6 and 60 μg/ml. This range was the maximum that provided minimal scatter in the standard error of the estimate (Sy.x) about the regression line. The working curve is seen to deviate from linearity by more than 2 σ at concentrations <6 μg/ml and > 60 μg/ml.

Considering the variance obtained as a function of concentration, Figure 2 plots the results for standard solutions.☆ Precision is seen to remain reasonable constant between 8 and 70 μg/ml but increases below 8. With an atmospheric sample extract and using linear regression for the working curve (Figure 3), the variance in observed sulfate increased

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☆The square root of the abscissa values are the standard deviations in chart units, where one chart unit corresponds to ca. .8 μg/ml sulfate.

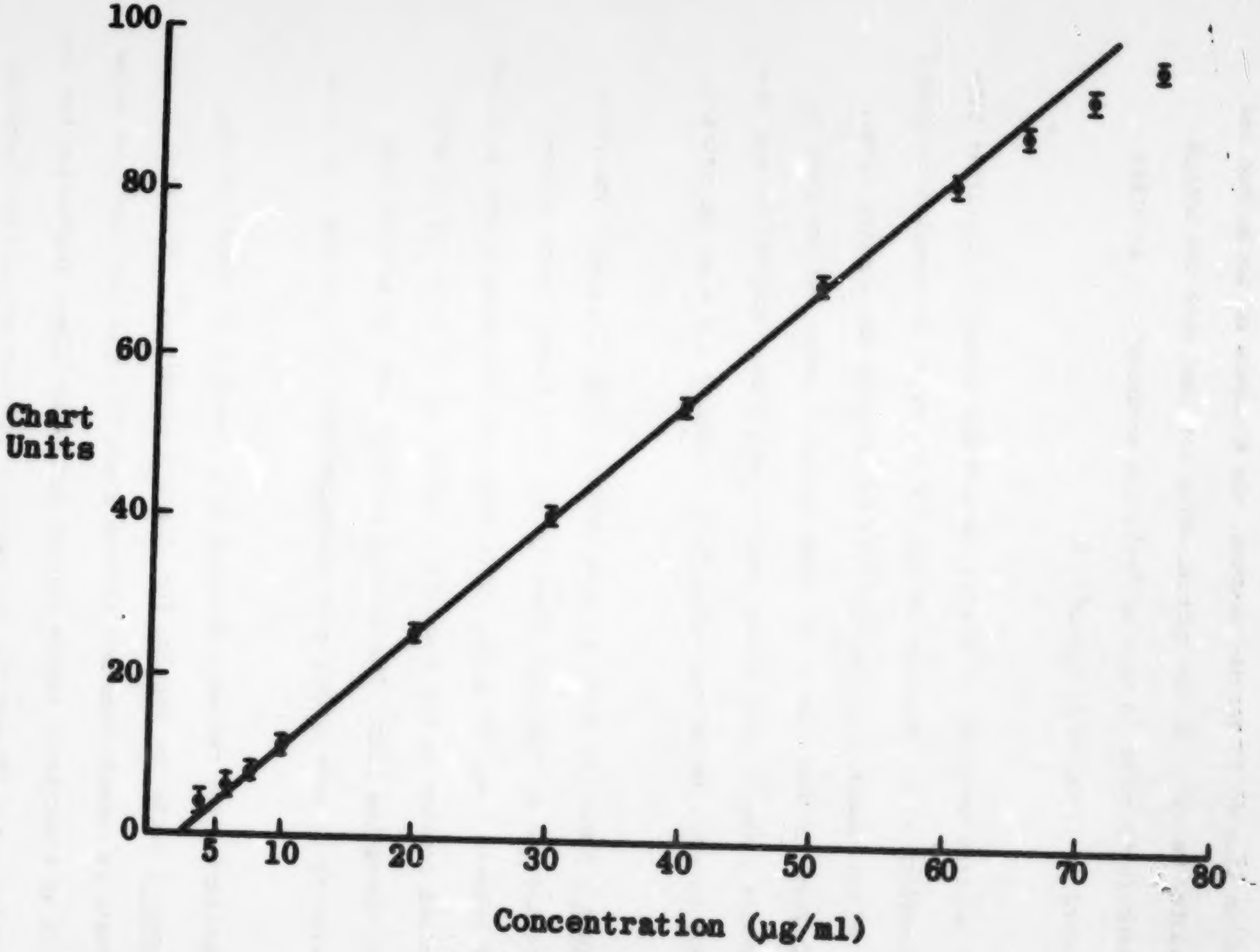


Figure 1. The working curve for the MTB method using linear regression fit for 6-60 µg/ml standards (error bars ± 2σ).

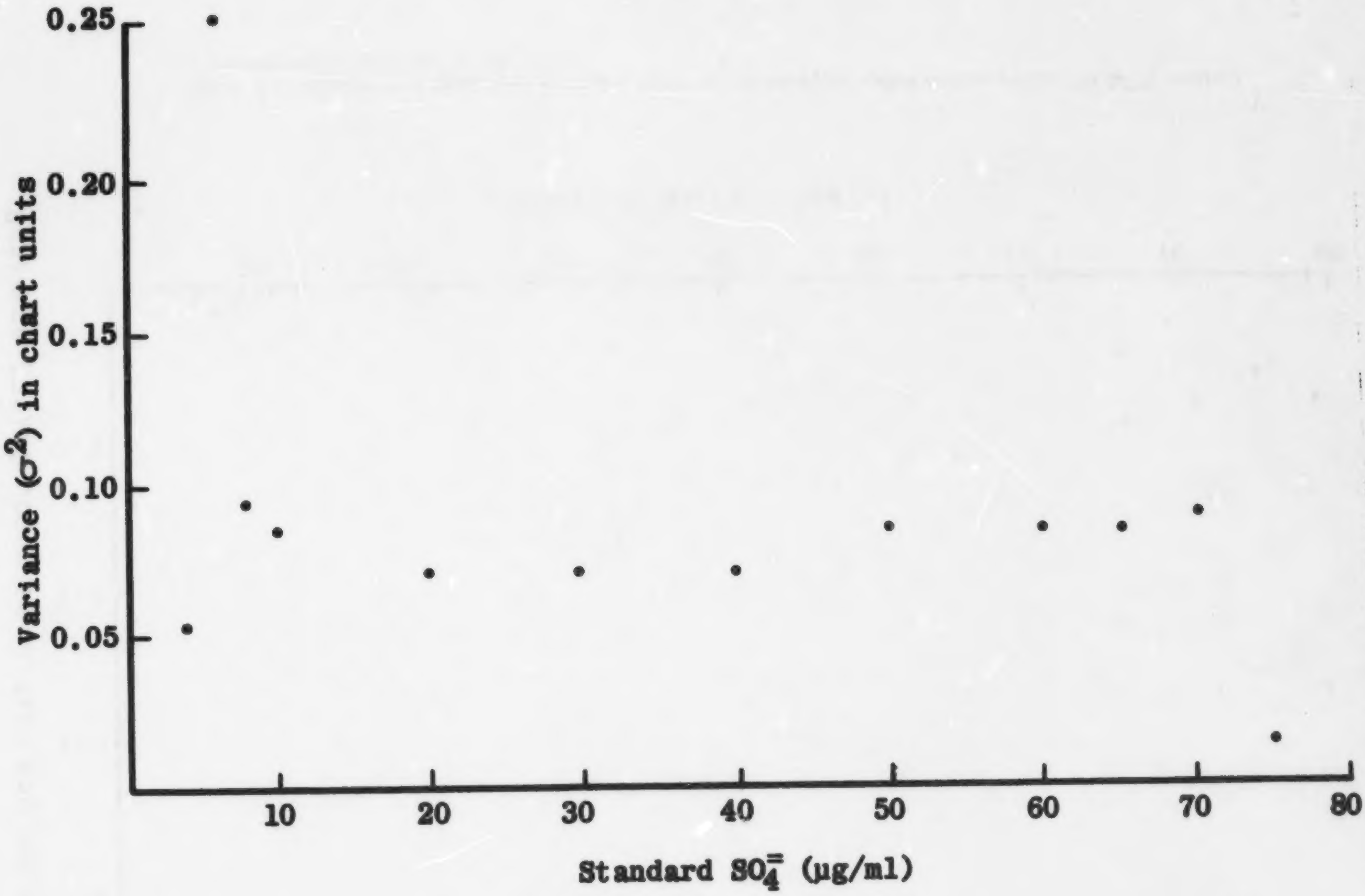


Figure 2. Variance of standard sulfate solution analyses versus concentration for the MTB method.

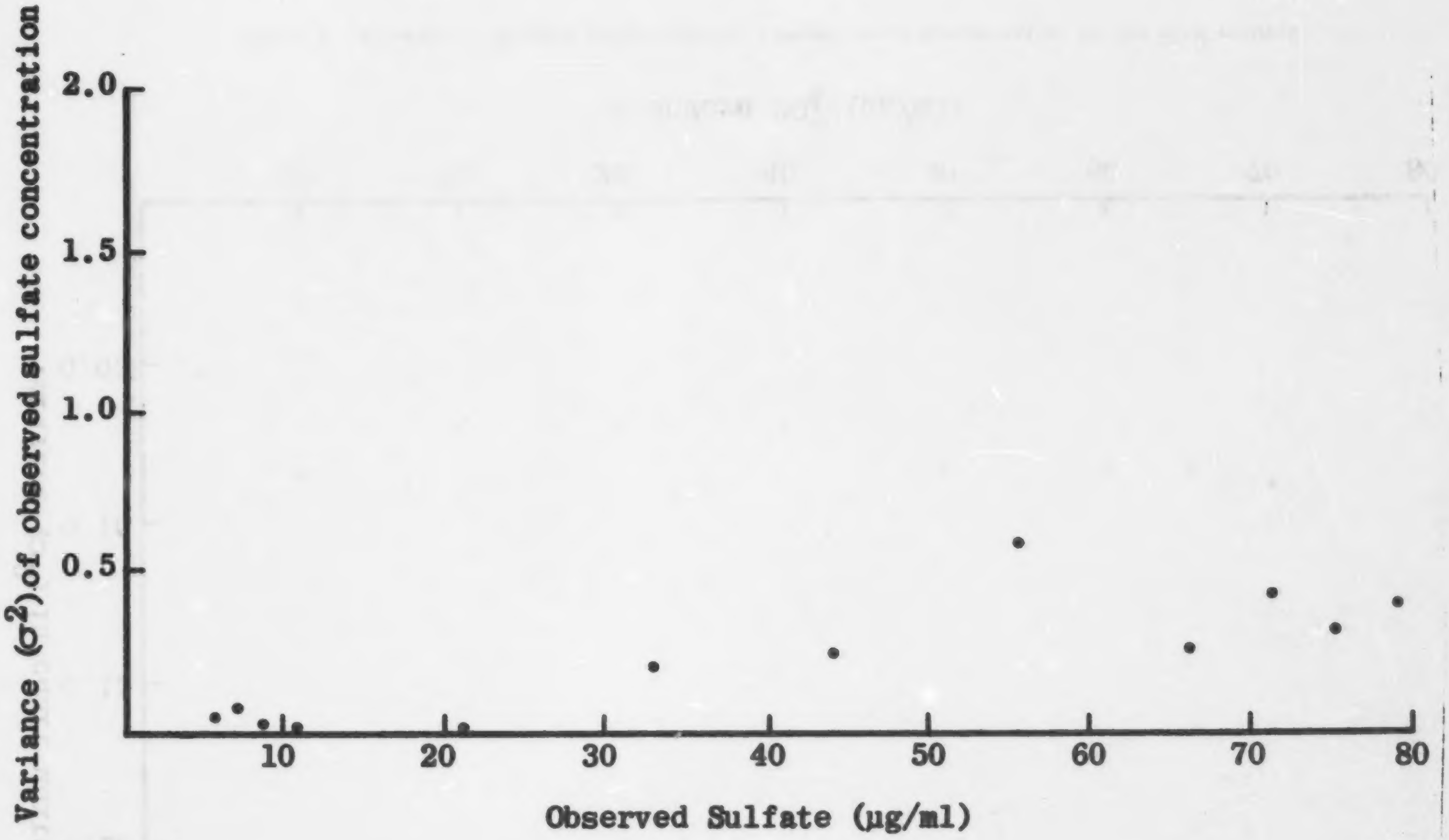


Figure 3. Variance of atmospheric sample extract sulfate analyses versus concentration for MTB method (linear regression 5-60 μg/ml fit).

with sulfate concentration, but never exceeds about 1.0% of the observed sulfate level from 4 to 75 μg/ml.

Table 1 and Figure 4 displays relative accuracy as a function of concentration with a single atmospheric extract diluted to varying degrees (using linear regression). The MTB method is seen to be accurate within 5% over the range 8.8 - 75 μg/ml relative to the accuracy at the mid-range concentration of the method.

The degree to which three regression equations fit the working curve can be evaluated by comparing actual sulfate concentrations for standards used in constructing the working curve to those obtained from a given regression line. Table 2 compares linear regression, a power function and a third order polynomial fit of the standards working curve. Results are shown separately for cases in which the 4 μg/ml standard was included or excluded from the regression line. The greatest deviation from the linear regression fit is at 4 μg/ml. Between 6 and 60 μg/ml, results are not greatly different for the three methods but the third order polynomial is, overall, somewhat better.

A comparison of relative accuracy between linear regression and the third order polynomial regresssion with atmospheric sample extracts is given in Table 3. As expected from the results with standards, below 6 μg/ml the results by linear regression are substantially

Table 1

## DETERMINATION OF RELATIVE ACCURACY WITH AN ATMOSPHERIC EXTRACT[a] - MTB METHOD

| Concentration, % of Undiluted | Observed $\mu g/ml^{b}$ | Calculated Undiluted Conc. $\mu g/ml^{c}$ | Expected Diluted Conc. $\mu g/ml^{e}$ | Observed Conc. / Expected Conc. |
|---|---|---|---|---|
| 75 | 79.2 | 105.6 | 83.9 | .945 |
| 70 | 75.4 | 107.7 | 78.3 | .963 |
| 65 | 71.5 | 110.1 | 72.7 | .985 |
| 60 | 66.6 | 111.0 | 67.1 | .993 |
| 50 | 55.7 | 111.4[d] | 55.9 | .997 |
| 40 | 44.2 | 110.5 | 44.7 | .988 |
| 30 | 33.0 | 110.2 | 33.6 | .985 |
| 20 | 21.2 | 106.1 | 22.4 | .948 |
| 10 | 11.0 | 110.0 | 11.2 | .983 |
| 8 | 8.79 | 109.8 | 8.95 | .982 |
| 6 | 7.08 | 118.0 | 6.71 | 1.055 |
| 4 | 5.61 | 140.3 | 4.47 | 1.255 |

a. St. Louis sample 618GH

b. Mean of three determinations.

c. Equals [(Observed)/(Concentration, % of undil.)] x (.01)

d. This value taken as the correct undiluted concentration.

e. Equals (correct undil conc.) x (conc., % of undil.) x (.01).

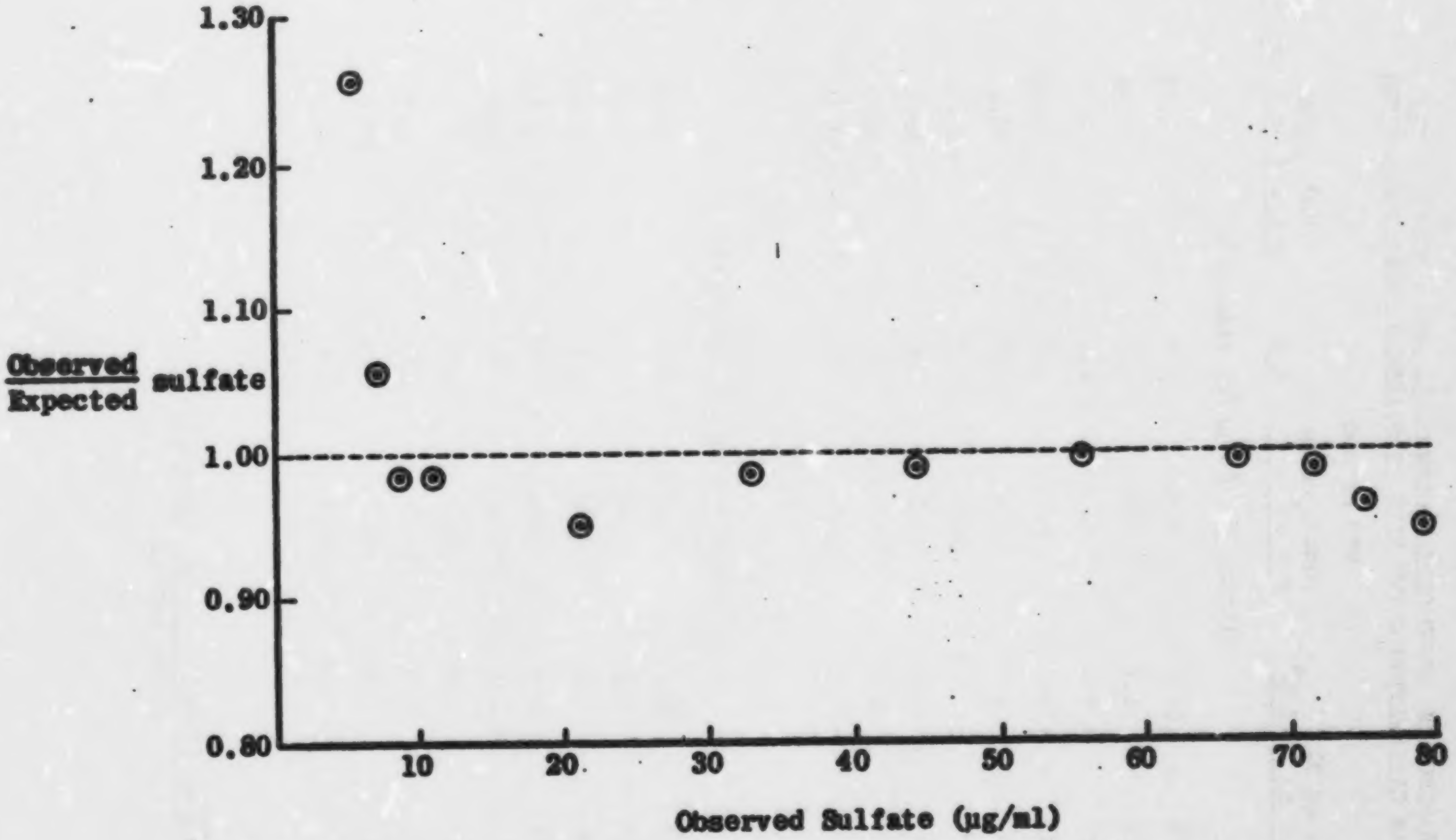


Figure 4. Accuracy of MTB method versus sulfate concentration from a single atmospheric sample extract (linear regression fit 5-60 µg/ml).

## Table 2

## COMPARISON OF THIRD ORDER POLYNOMIAL, POWER FUNCTION AND LINEAR CALIBRATION CURVE FITS ON STANDARD SULFATE SOLUTIONS

### MTB METHOD

| Actual µg/ml | Found, µg/ml $y = a + bx$ | Δ %a) | Found, µg/ml $y = ax^b$ | Δ % | Found, µg/ml $y = a + bx + cx^2 + dx^3$ | Δ % |
|---|---|---|---|---|---|---|
| **Fitting 4 - 60 µg/ml standards** | | | | | | |
| 4 | 4.66 | 16.6 | 4.19 | 4.8 | 4.28 | 7.0 |
| 6 | 6.10 | 1.7 | 5.89 | - 1.8 | 5.98 | - .37 |
| 8 | 7.66 | - 4.2 | 7.67 | - 4.1 | 7.76 | - 3.0 |
| 10 | 9.53 | - 4.7 | 9.75 | - 2.5 | 9.82 | - 1.8 |
| 20 | 19.6 | - 1.8 | 20.4 | 2.0 | 20.2 | .91 |
| 30 | 30.0 | - .04 | 30.7 | 2.3 | 30.1 | .20 |
| 40 | 40.4 | 1.01 | 40.7 | 1.8 | 39.9 | - .21 |
| 50 | 50.5 | 1.04 | 50.2 | .42 | 50.0 | - .050 |
| 60 | 59.5 | - .85 | 58.5 | - 2.6 | 60.0 | - .050 |
| **Fitting 6 - 60 µg/ml standards** | | | | | | |
| 4 | 4.87 | 21.8 | 4.31 | 7.8 | 4.55 | 13.6 |
| 6 | 6.30 | 5.1 | 6.03 | .50 | 6.17 | 2.8 |
| 8 | 7.86 | - 1.8 | 7.82 | - 2.2 | 7.88 | - 1.5 |
| 10 | 9.71 | - 2.9 | 9.91 | - .93 | 9.88 | - 1.2 |
| 20 | 19.8 | - 1.2 | 20.5 | 2.6 | 20.1 | .52 |
| 30 | 30.1 | .20 | 30.7 | 2.4 | 30.0 | .013 |
| 40 | 40.4 | 1.05 | 40.6 | 1.4 | 39.9 | - .16 |
| 50 | 50.5 | .96 | 49.9 | - .24 | 50.0 | .077 |
| 60 | 59.4 | - .99 | 58.0 | - 3.4 | 60.0 | - .014 |

---

a) $\Delta \% = 100 \times \frac{\mu g/ml \text{ (found)} - \mu g/ml \text{ (actual)}}{\mu g/ml \text{ (actual)}}$

## Table 3

### COMPARISON OF THIRD ORDER POLYNOMIAL AND LINEAR CALIBRATION CURVE FITS ON ATMOSPHERIC SAMPLE EXTRACTS[a]

### MTB METHOD

| Expected µg/ml | Found, Linear Regression, µg/ml[b] | Δ %[c] | Found, 3rd Order Regression, µg/ml[d] | Δ %[c] |
|---|---|---|---|---|
| 4.47 | 5.61 ± 0.22 | 25.5 | 4.64 ± 0.40 | 3.8 |
| 6.71 | 7.08 ± 0.27 | 5.5 | 6.48 ± 0.37 | - 3.4 |
| 8.95 | 8.79 ± 0.14 | - 1.8 | 8.53 ± 0.25 | - 4.7 |
| 11.2 | 11.0 ± 0.12 | - 1.7 | 11.1 ± 0.13 | - 0.7 |
| 22.4 | 21.2 ± 0.05 | - 5.1 | 22.0 ± 0.09 | - 1.6 |
| 33.6 | 33.0 ± 0.45 | - 1.5 | 33.6 ± 0.53 | 0.06 |
| 44.7 | 44.2 ± 0.50 | - 1.2 | 44.1 ± 0.57 | - 1.3 |
| 55.9 | 55.7 ± 0.77 | - 0.4 | 55.3 ± 0.70 | - 0.98 |
| 67.1 | 66.6 ± 0.50 | - 0.7 | 66.7 ± 0.12 | - 0.54 |
| 72.7 | 71.6 ± 0.65 | - 1.5 | 72.6 ± 0.30 | - 0.18 |
| 78.3 | 75.4 ± 0.57 | - 3.7 | 77.5 ± 0.69 | - 1.01 |
| 83.9 | 79.2 ± 0.63 | - 5.5 | 82.1 ± 1.2 | - 2.1 |

---

a. A glass fiber hi-vol extract from St. Louis was used with the initial concentration of 112 µg/ml as measured in the optimal concentration range of method (ca. 35 µg/ml). Expected concentrations were based on this value and the degree of dilution used. Linear regression was used for the working curve in calculating expected concentrations.

b. Mean of three trials with standard deviation.

c. $$\Delta \% = \frac{\mu g/ml\ (found) - \mu g/ml\ (expected)}{\mu g/ml\ (expected)} \times 100$$

d. $y = a + bx + cx^2 + dx^3$

high. Between 6 and 80 μg/ml, linear regression is accurate within 6%, whereas the third order polynomial is somewhat more accurate over a wider range of concentrations.

The conclusions from the above are as follows:

1. The best linear regression fit (the fit which minimized Sy.x) of the working curve for the MTB method encompasses the range 6 to 60 μg/ml.
2. The range of constant variance for the MTB method using standard solutions has a lower limit betwen 6 - 8 μg/ml and an upper limit between 70 - 75 μg/ml. The variance observed for atmospheric extracts was considered constant throughout the range investigated, 5 - 80 μg/ml.
3. The concentration range of acceptable accuracy for the MTB method depends to some degree upon the regression technique used to fit the working curve. Based on atmospheric extracts as well as standard solutions, the working range employing linear regression (5-6 to 60 μg/ml fit) can be considered to be 7 - 75 μg/ml if < 5.5% error is acceptable. The lower end of the working range can be extended down to approximately 4 μg/ml with ≤ 7% error by using a third order polynomial fit.

### C. Accuracy Using EPA Audit Strips

EPA audit sulfate samples prepared by Columbia Scientific, Inc. (CSI) as glass fiber filter strips spiked with potassium sulfate were provided by the EPA/RTP laboratory. These were extracted in distilled $H_2O$ (final volume 50 ml) by refluxing for 90 minutes. Based on the reported range for the samples, 1000-6000 μg/strip, a concentration range from 20 to 120 μg/ml was expected, except for blanks. Accordingly, all extracts were diluted by a factor of two before analysis. Table 4 compares the MTB results to those obtained at Research Triangle Park using the $BaCl_2$ turbidimetric method (which were reportedly in excellent agreement with CSI's theoretical values). The MTB results averaged 7% low.

## Table 4

## COMPARISON OF MTB AND EPA RESULTS FOR SRM $K_2SO_4$ DOPED STRIPS (µg/strip)

| Sample | MTB[a] | EPA ($BaCl_2$ Turbidimetric)[b] | MTB/EPA |
|---|---|---|---|
| 3000 series | 2258 ± 5 | 2400 ± 81 | 0.941 |
| 4000 series | 5757 ± 124 | 6400 ± 128 | 0.900 |
| 5000 series (blank) | 205 ± 2 | 30 to 110 | — |
| 6000 series | 455 ± 5 | 480 ± 80 | 0.948 |
| 9000 series | 1384 ± 11 | 1500 ± 85 | 0.923 |

Mean Ratio MTB/EPA (turbidimetric) = 0.93[c]

---

[a] Mean of 4 strips ± standard deviation of the mean.

[b] J. Puzak, private communication, 1976. Excepting the blanks, the values cited were reported to be in excellent agreement with theoretical values provided by Columbia Scientific.

[c] Excludes blanks.

## IV. EVALUATION OF THE SEMI-AUTOMATED MODIFIED BROSSET METHOD

### A. Analytical Protocol

In the first year of this study, a manual, modified Brosset method which used the solvents acetone or dioxane was evaluated. For the current program, equipment similar to that in Brosset's laboratory was acquired. The solvent was changed to isopropyl alcohol based on favorable results observed with this solvent in studies performed at RTP. A detailed protocol for the method is included as Appendix C.

### B. Preliminary Evaluation and Accuracy Using EPA Audit Strips

The method requires removal of cationic interferents by ion exchange. Initial trials were made using Rexyn 101 (H) ion exchange resin. The precision of the method proved to be excellent (better than 1% C.V.) with standard solutions and the working curve reproducible. However, initial comparisons with the MTB method using extracts from atmospheric samples as well as extracts from the $K_2SO_4$ doped strips demonstrated results which were 15-20% higher. The problem was traced to the ion exchange resin which liberates a material analyzed as sulfate in spite of extensive prewashings. For example, 50 cc of resin mixed with 50 cc water released what corresponded to 150 μg sulfate after prolonged soaking.

Standard sulfate solutions showed < 1% change in concentration by passing through resin columns which had been used 6 times previously.

While sufficient washing may eliminate or minimize the problem, on the advice of EPA personnel, the resin was changed to AG 50-W-X8, 50 - 100 mesh and the system re-evaluated.

Using the new resin, the extracts from 5 of the $K_2SO_4$ loaded strips, previously analyzed by the MTB method, were reanalyzed. The system was calibrated using sodium sulfate run in duplicate before and after the measurement of these EPA audit samples. The mean regression line was then used as calculated from four values obtained for each concentration of the standard solutions. Results are shown in Table 5 for the means of two determinations of each sample.

In general, the Brosset results agree more closely with the EPA findings than did the MTB. Excluding the blank value, the ratio of means differed by only 4% with Brosset higher.

## C. Working Range

The protocol followed in evaluating the working range of the modified Brosset method is similar to that detailed for the MTB method (Appendix B).

### 1. Linearity of Working Curve and Reproducibility

Three trials were run on separate days, and the three working curves plotted separately. Figure 5 shows the working curve obtained with the first of three trials. The curve is distinctly non-linear above 14 $\mu$g/ml and expected result because of the limited capacity of the reagent. It is also somewhat non-linear

## Table 5

### SULFATE DETERMINATION OF SRM FILTER STRIPS WITH THE BROSSET METHOD (μg/strip)

| Sample ID | Brosset | EPA Value[a] | Brosset/EPA |
|---|---|---|---|
| 3105 | 2439 ± 8 | 2400 ± 81 | 1.02 |
| 4145 | 6280 ± 66 | 6400 ± 128 | 0.981 |
| 5337 (blank) | 36 ± 1.4 | 30 to 110 | --- |
| 6112 | 516 ± 6 | 480 ± 80 | 1.08 |
| 9200 | 1620 ± 26 | 1500 ± 85 | 1.08 |

Mean ratio Brosset/EPA (turbidimetric) = 1.04[b]

---

[a] Using the $BaCl_2$ turbidimetric method

[b] Excludes blank

[c] Duplicate analyses of single strip extract

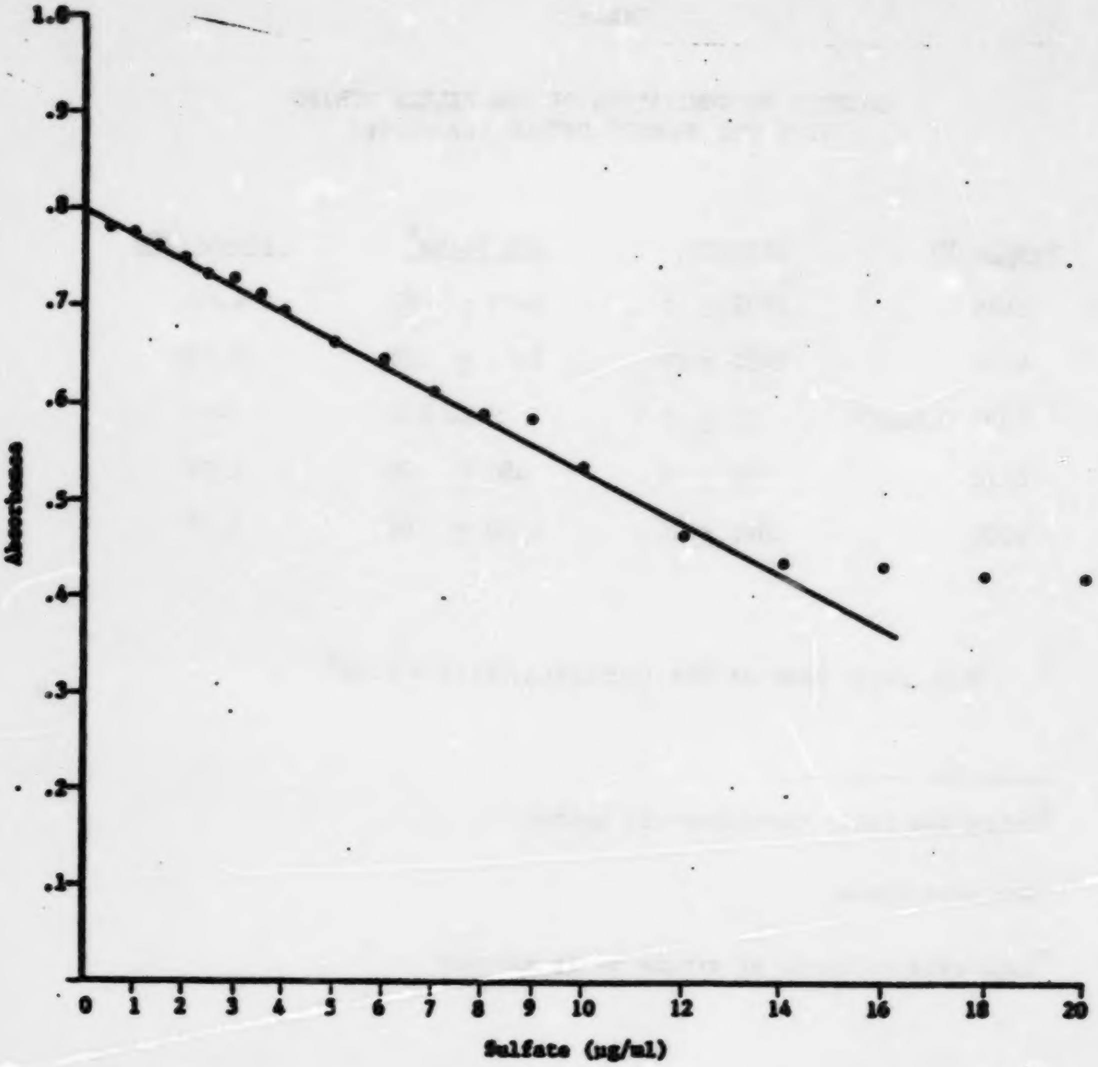


Figure 5. Working curve for the modified Brosset method (Trial A).

below 1 μg/ml. The goodness of fit to a straight line is tested for the three trials in Table 6. As suggested both by this table and by Figure 5, the value of Sy.x increased markedly above 14 μg/ml. The three working curves determined on separate days and in differing sequences were not significantly different, by analysis of covariance, implying reasonable precision with standards.

2. Precision and Accuracy with Atmospheric Samples

Extract from three hi-vol samples, one each from Durham, NC., St. Louis, MO, and Pasadena, CA, were analyzed. Each extract was diluted to provide 14 concentrations between approximately 0.5 and 20 μg/ml. Relative accuracy was established from one trial with each of these three extracts. Precision as a function of concentration employed three determinations (done on separate days) with the St. Louis sample extract.

Relative accuracy was defined in paragraph III, B. The expected concentration was based upon analyses done with solutions in the 6-9 μg/ml range. Table 7 shows, for one of the hi-vol sample extracts, the observed concentrations and the concentration of the undiluted solution calculated from each analysis. In this case, the value calculated from the 6.7 and 9.1 μg/ml solutions were averaged, and the resulting 22.56 μg/ml was accepted as the undiluted extract concentration. Expected values were then calculated from this and the percent dilution. Results are shown for the extracts from the three atmospheric samples in Figure 6. With the Durham and

## TABLE 6

## STANDARD ERROR OF THE ESTIMATE (Sy.x) FOR WORKING CURVES BY THE MODIFIED BROSSET METHOD

| | | Trial[d] | |
|---|---|---|---|
| **Range of Standards (μg/ml)** | A[a] | B[b] | C[c] |
| 0-8 | .00302 | .00516 | .0106 |
| 0-9 | .00336 | --- | .0105 |
| 0-10 | .00330 | .00519 | .0103 |
| 0-12 | .00455 | .00518 | .0103 |
| 0-14 | .00484 | .00571 | .0102 |
| 0-16 | .0104 | .0118 | .0131 |
| 0-18 | .0163 | .0183 | .0203 |
| 0-20 | .0234 | .0261 | .0289 |

---

a. Standards run in succession, 0, 1, 2, 3 .........20 μg/ml

b. Standards run in succession 20, 19, 18 .......... 0 μg/ml

c. Standards run in random sequence

d. By analysis of covariance the curves from trials A, B and C are not significantly different at the 95% level (F = 0.16).

## TABLE 7

## DETERMINATION OF RELATIVE ACCURACY WITH AN ATMOSPHERIC EXTRACT[a] MODIFIED BROSSET METHOD

| Concentration, % of Undiluted | Observed µg/ml | Calculated Undiluted Conc. µg/ml[b] | Expected Diluted Conc. µg/ml[d] | Observed Conc. / Expected Conc. |
|---|---|---|---|---|
| 100 | 13.4 | 13.4 | 22.6 | 0.594 |
| 80 | 13.5 | 16.9 | 18.1 | 0.747 |
| 70 | 13.6 | 19.4 | 15.8 | 0.861 |
| 60 | 13.6 | 22.7 | 13.5 | 1.00 |
| 50 | 11.9 | 23.8 | 11.3 | 1.05 |
| 40 | 9.09 | 22.7[c] | 9.02 | 1.01 |
| 30 | 6.72 | 22.4[c] | 6.77 | 0.992 |
| 25 | 5.53 | 22.1 | 5.64 | 0.980 |
| 20 | 4.52 | 22.6 | 4.51 | 1.00 |
| 15 | 3.33 | 22.2 | 3.38 | 0.985 |
| 10 | 2.26 | 22.6 | 2.26 | 1.00 |
| 7.5 | 1.74 | 23.2 | 1.69 | 1.03 |
| 5 | 1.07 | 21.3 | 1.13 | 0.946 |
| 2.5 | 0.47 | 18.9 | 0.56 | 0.84 |

---

[a] Durham, N.C. sample N 23076.

[b] Equals (Observed) x (Concentration, % of undil.) x (0.01).

[c] The mean of these values accepted as the correct undiluted concentration.

[d] Equals (correct undil. conc.) x (conc., % of undil.) x (0.01).

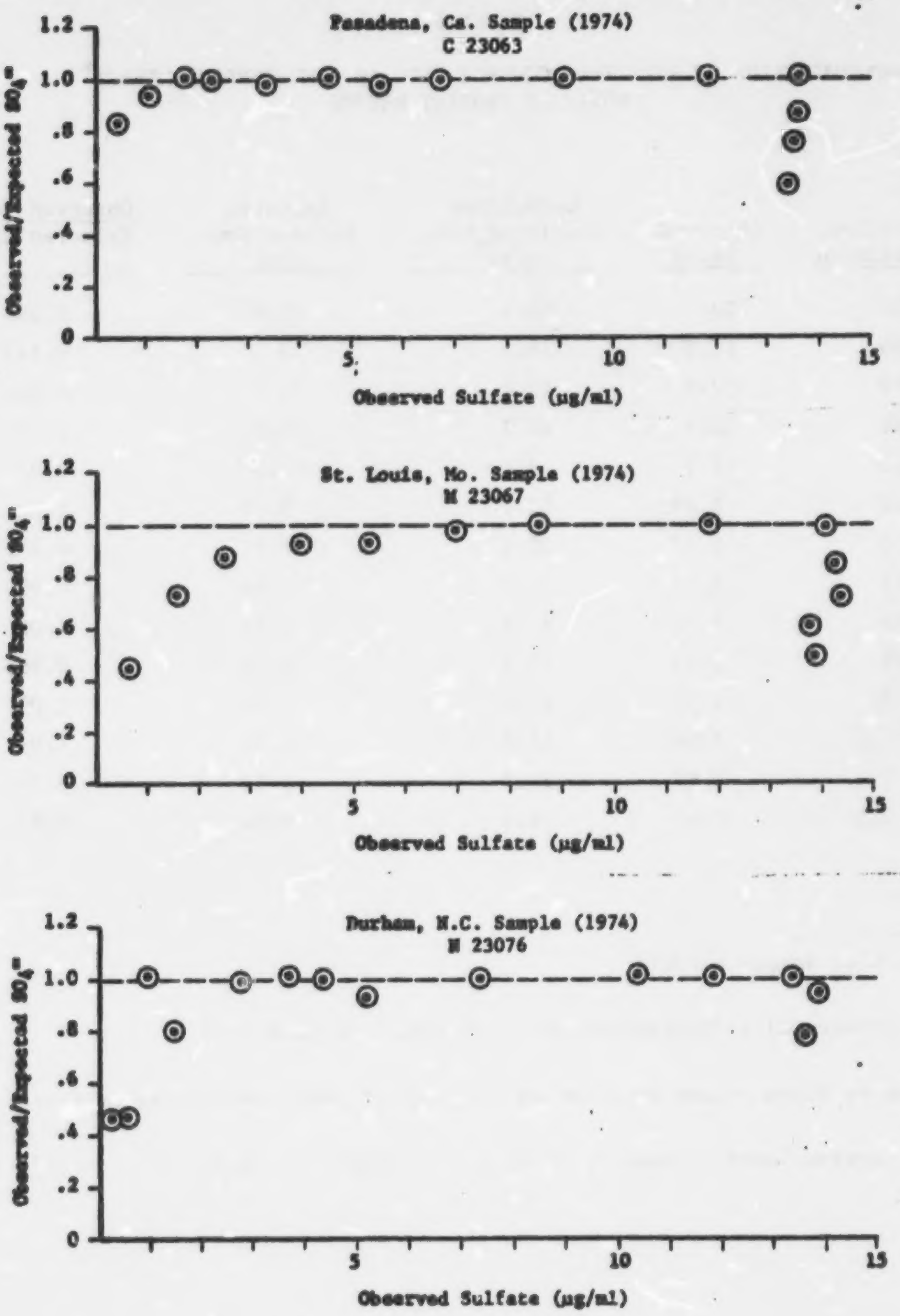


Figure 6. Relative accuracy by the modified Brosset method with atmospheric samples.

Pasadena samples, accuracy appears acceptable in the range 3-13 μg/ml. With the St. Louis sample (from the first year of this study) which was notable for its high level of calcium, relative accuracy within 5% is observed in the range 7-14 μg/ml.

Finally, Figure 7 plots the variance from three determinations at each concentration level for the St. Louis sample diluted to varying degrees. Below 2.6 μg/ml, the variance increased markedly. In the range 2.6-14 μg/ml, the variance is both small and relatively constant excepting the sample at about 7 μg/ml. The variance in this case corresponds to a coefficient of variation of about 3%. There is no apparent explanation for this outlier.

A principal source of the variance observed appears to be the changes in absorbance readings with time. To minimize this effect, the spectrophotometer was reset to read 0.800 with a reagent blank following every third determination. Nevertheless, just prior to resetting, the reagent blank typically changed about 0.004 absorbance units. A change of this magnitude corresponds to about 0.2 μg/ml. The data point at 7 μg/ml, had the following absorbance values and corresponding concentrations in three trials:

| Absorbance | μg/ml $SO_4^{=}$ |
|---|---|
| .616 | 6.90 |
| .612 | 7.08 |
| .620 | 6.70 |

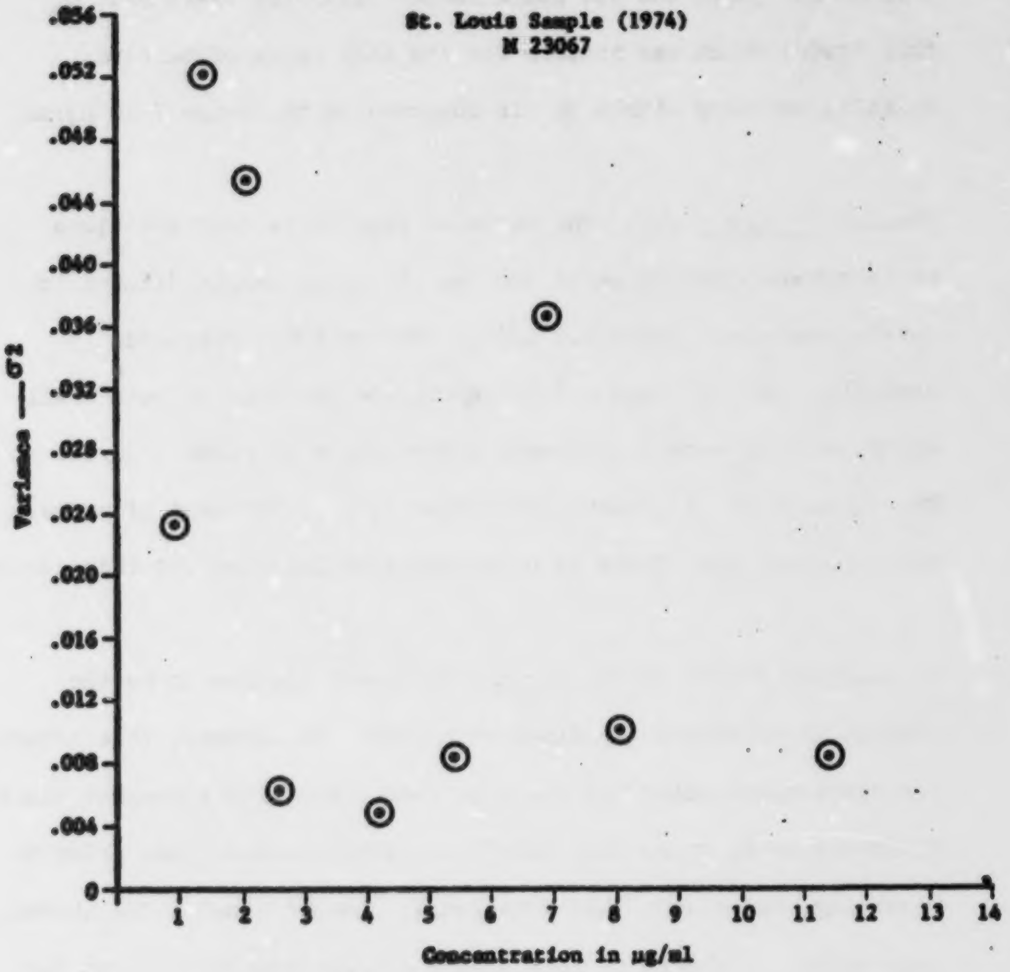


Figure 7. The variance of sulfate determinations on an atmospheric sample with the modified Brosset method.

These findings are consistent with the ± 0.2 μg/ml value claimed for precision by C. Brosset.

Conclusions from the above are the following:

a. The working curve of the modified Brosset method can be treated by linear regression in the range 0-14 μg/ml with acceptable goodness of fit.

b. The working curve is reproducible from day to day.

c. The relative accuracy of the modified Brosset method with atmospheric samples was constant within 5% over the range 3-13 μg/ml with two of three samples. A more restricted range for a St. Louis sample 7-14 μg/ml suggests that the presence of other ions can influence the relative accuracy of the method.

d. The variance for analysis in triplicate for the St. Louis samples remained approximately constant in the range 2.6-14 μg/ml with one exception.

e. Based on both accuracy and precision, the working range of the modified Brosset procedure is calculated to be 3-13 μg/ml.

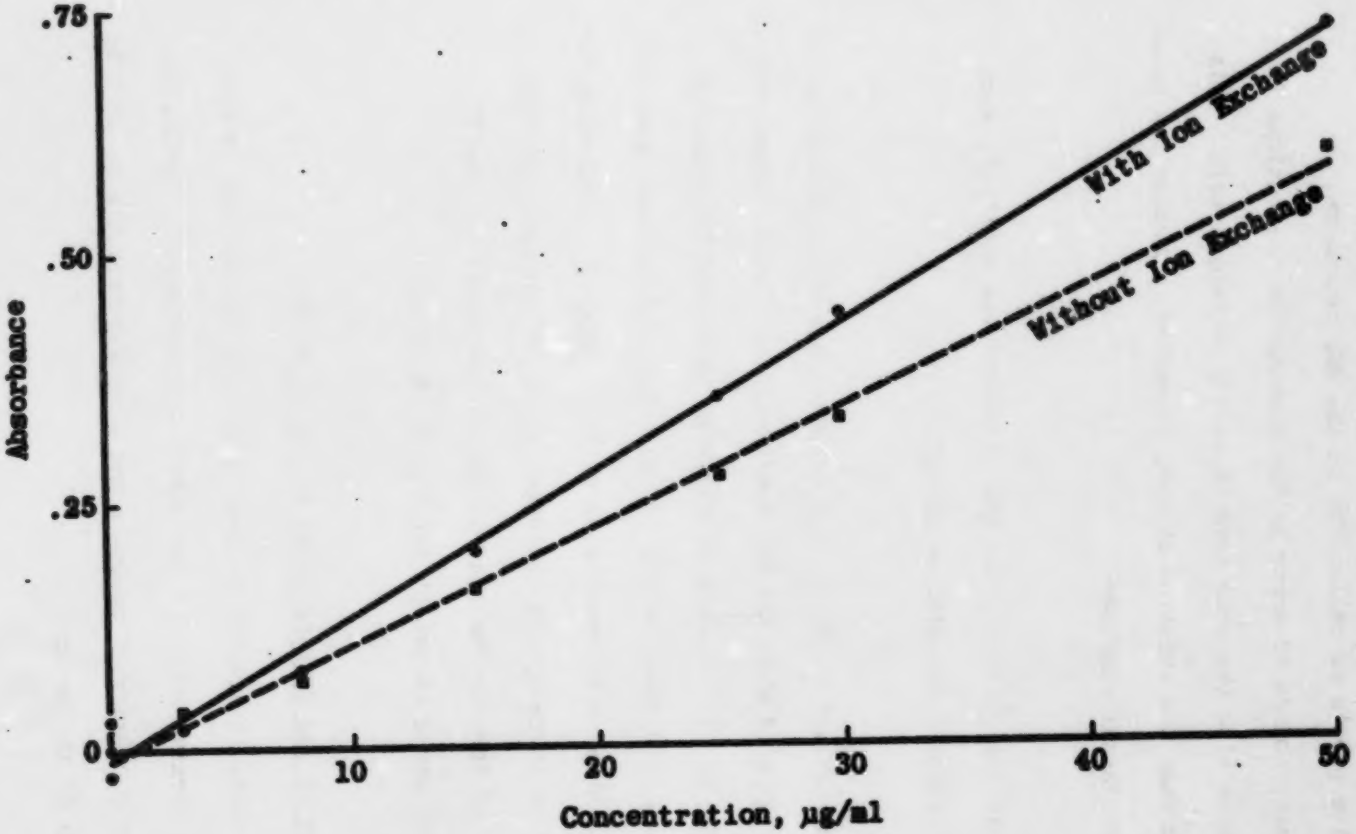
f. The coefficient of variation in the 2.6-14 μg/ml range was, in all cases, ≤ 3%.

## V. EVALUATION OF THE MANUAL BARIUM CHLORANILIATE (BC) METHOD

### A. Protocol and Preliminary Evaluation

A protocol for conducting manual BC determinations was prepared, under EPA sponsorship, by Midwest Research Institute (MRI) and is included as Appendix D. Initial efforts at AIHL to follow this protocol revealed a number of shortcomings as follows:

1. Plastic containers are leached by isopropyl alcohol. Blanks and standards made with isopropyl alcohol stored for several days in these containers had unacceptable scatter.
2. The standard curve without ion exchange was different than that obtained when ion exchange was included (see Figure 8), possibly an effect caused by some organics bleeding from the resin. Control of contact time between standards and resin was very important to obtain reproducible results.
3. Filtration with washed fritted funnels gave highly scattered results. This could be avoided by not washing the frit. Sample carry-over was eliminated by rinsing the frit with about 7-8 ml of the next sample solution,discarding this portion and then collecting the remainder of the new sample. This procedure gave better results than using fine pore filter paper (Whatman 42) and filtering by gravity. Chloranilate accumulated on the frit was removed by scraping and an IPA rinse. An alternative technique involving use of a disposable glass fiber filter above the frit proved to yield less precise results than by the scraping procedure.



**Without Ion Exchange**

ABS = .0119 [Conc.] − .0122

r = .998

Sy·x = .0140

**With Ion Exchange**

ABS = .0146 [Conc.] − .0115

r = .997

Sy·x = .0207

Figure 8. Barium chloranilate calibrations with and without ion exchange, May 25, 1976.

4. Use of glass pipets gave better precision than using plastic repetitive pipets as called for in the MRI procedure.
5. A potential source of error is the exchange of the cations in the samples with the acid form of an ion exchange resin. This will decrease the solution pH and, therefore, increase the solubility of Ba-chloranilate.

Based on these observations, the MRI procedure was modified, with the revised protocol included as Appendix E.

Following the revised protocol, the accuracy and precision of the BC method was evaluated with the EPA audit sulfate strips. Three filter strips at each of five sulfate levels were extracted by refluxing for 90 minutes with final volume 100 ml. Each extract was analyzed with a single trial with results as shown in Table 8. Comparing the AIHL results to those by EPA indicates that, on average, the AIHL results were 1% lower. The coefficient of variation for the BC determinations was < 4% except for the blank strips.

## B. Determination of the Working Range of the BC Method

Following a protocol similar to that used with the MTB and Brosset methods, the working range of the method was evaluated. Again, the criteria were constancy of variance and accuracy relative to that in the mid-range of the method.

## TABLE 8

## ACCURACY OF THE BARIUM CHLORANILATE (BC) METHOD USING EPA AUDIT SULFATE STRIPS (μg/STRIP)[a]

| Sample ID | Observed[b] | Mean ± 1 σ | Theoretical[a] | EPA Value by a Modified BC Method | AIHL(BC)/ EPA(BC) |
|---|---|---|---|---|---|
| 2058 | 6364 | 6372 ± 111 | 6549 | 6585 | 0.973 |
| 2059 | 6486 | | | | |
| 2060 | 6265 | | | | |
| 3040 | 129 | | | | |
| 3041 | 58 | 81 ± 41 | 0.0 | 20 | --- |
| 3042 | 58 | | | | |
| 5048 | 2773 | | | | |
| 5049 | 2602 | 2707 ± 92 | 2670 | 2653 | 1.01 |
| 5050 | 2745 | | | | |
| 7035 | 4120 | | | | |
| 7036 | 4141 | 4149 ± 33 | 4240 | 4252 | 0.979 |
| 7037 | 4184 | | | | |
| 8060 | 1754 | | | | |
| 8061 | 1654 | 1728 ± 65 | 1737 | 1766 | 0.995 |
| 8062 | 1775 | | | | |

Mean Ratio AIHL/EPA = 0.99[c]

a. Glass fiber filter strip spiked with known quantities of $K_2SO_4$ by Columbia Scientific.

b. Extracted by refluxing for 90 minutes; final volume 100 ml.

c. Excluding blank samples.

The working curve with ion exchange pretreatment was replicated. By analysis of covariance, the results for three curves were not significantly different. The resulting pooled curve is shown in Figure 9.

Table 9 summarizes results for the observed concentrations and the concentrations of the undiluted solution calculated from each analysis. In this case, the value calculated from the 11, 24, and 38 μg/ml solutions were averaged and the resulting 60.67 μg/ml accepted as the undiluted extract concentration. Expected values were then calculated from this and the % dilution. Also shown is the variance ($\sigma^2$) for the three determinations of each observed concentration. The ratio of observed to expected concentrations are plotted against observed concentrations for three determinations on the same particulate extract in Figure 10. Relative accuracy within ± 5% was observed in the range 12-51 μg/ml.

Figure 11 plots the variance from three determinations at each concentration level for the Durham sample diluted to varying degrees. The variance remains low and approximately constant up to 38 μg/ml; at higher levels, the variance increases markedly. At 51 μg/ml, the variance observed corresponds to a coefficient of variation of 6%.

Based on both the observed precision and accuracy, the working curve covers the range from about 10 to 40 μg/ml. However, if a coefficient of variation of 6% is acceptable then a range from about 10 to 50 μg/ml is indicated.

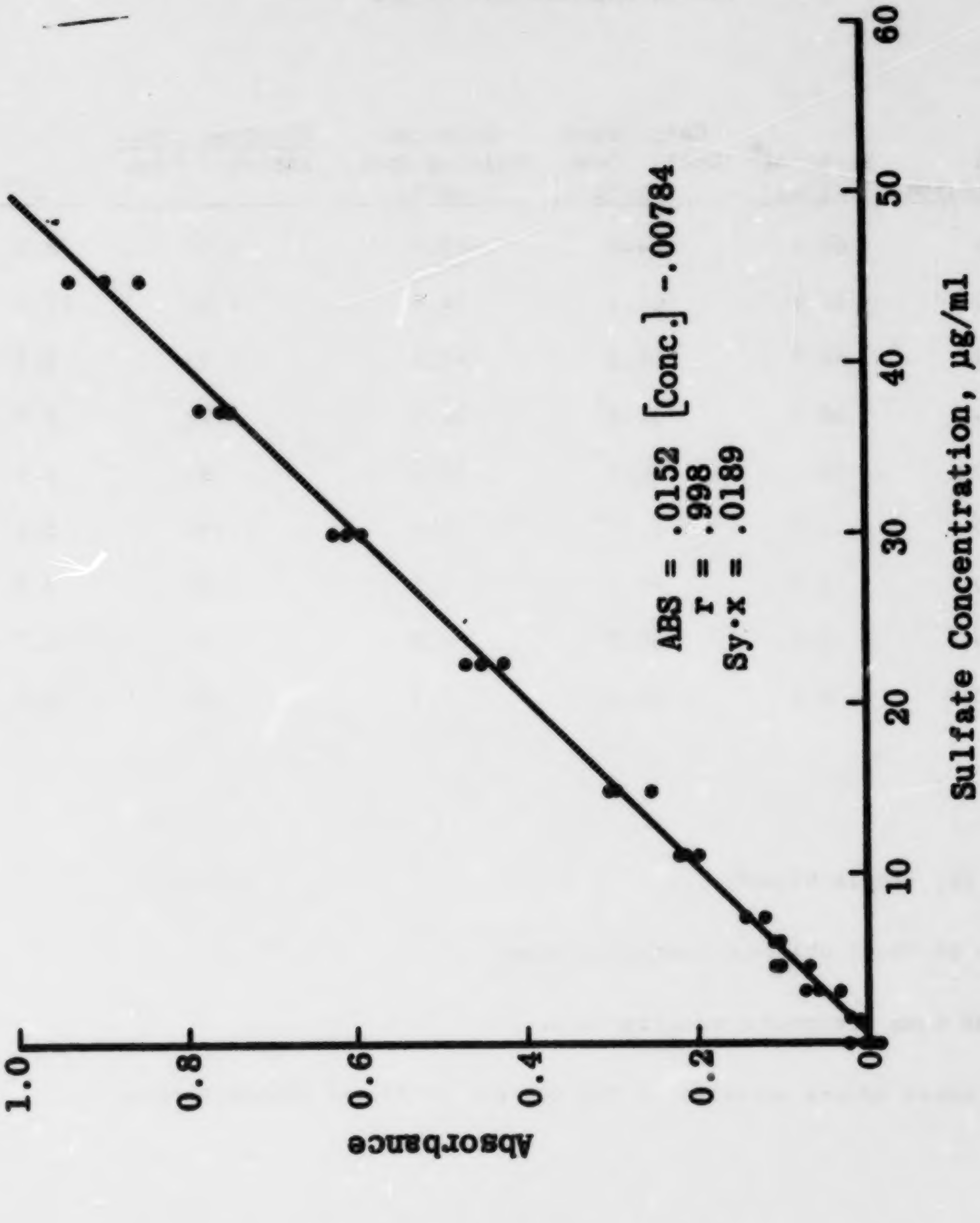


Figure 9. Chloranilate method calibration.

## TABLE 9

## DETERMINATION OF RELATIVE ACCURACY AND PRECISION WITH AN ATMOSPHERIC EXTRACT[a]

### BARIUM CHLORANILATE METHOD

| Conc. % of Undiluted | Observed[b] µg/ml | Calculated Undil. Conc. µg/ml | Expected Diluted Conc. µg/ml | Observed Conc. / Expected Conc. | $\sigma^2$[c] |
|---|---|---|---|---|---|
| 100 | 64.8 | 64.8 | 60.7 | 1.07 | 14.5 |
| 90 | 57.9 | 64.4 | 54.6 | 1.06 | 17.0 |
| 80 | 50.8 | 63.5 | 48.5 | 1.05 | 8.9 |
| 60 | 38.1 | 63.5[d] | 36.4 | 1.05 | 1.9 |
| 40 | 24.1 | 60.3[d] | 24.3 | .99 | 2.6 |
| 20 | 11.6 | 58.2[d] | 12.1 | .96 | 3.3 |
| 10 | 4.9 | 49.5 | 6.1 | .82 | 0.3 |
| 5 | 1.5 | 30.5 | 3.0 | .50 | 1.7 |
| 2.5 | - 0.9 | - 37.3 | 1.5 | - .61 | 0.8 |

[a] Durham, NC, sample N23069.

[b] The mean of the 3 observed concentrations.

[c] $\sigma^2$ of the mean observed concentrations.

[d] Mean of these values accepted as the correct undiluted concentration.

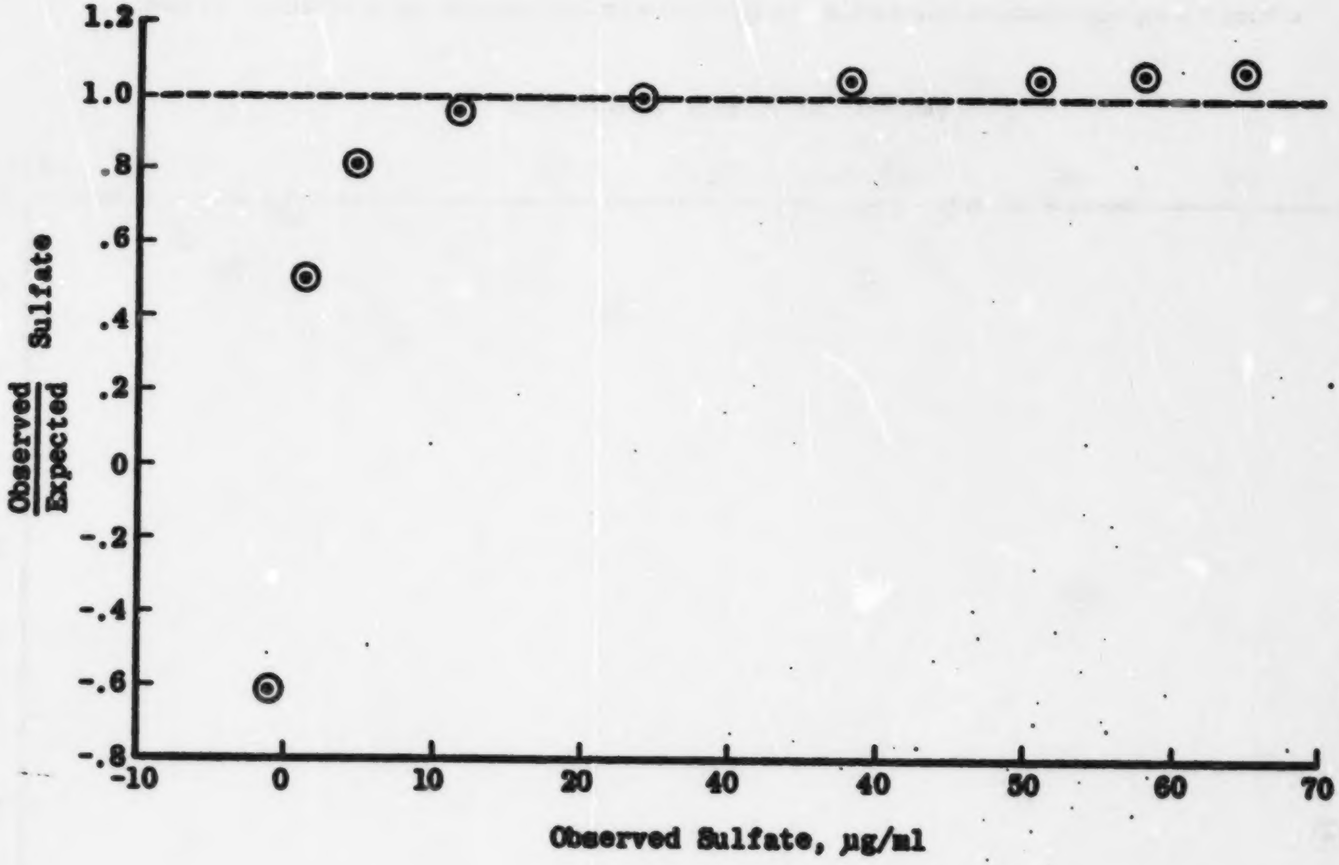


Figure 10. Accuracy of barium chloranilate versus sulfate concentration from a single atmospheric sample extract.

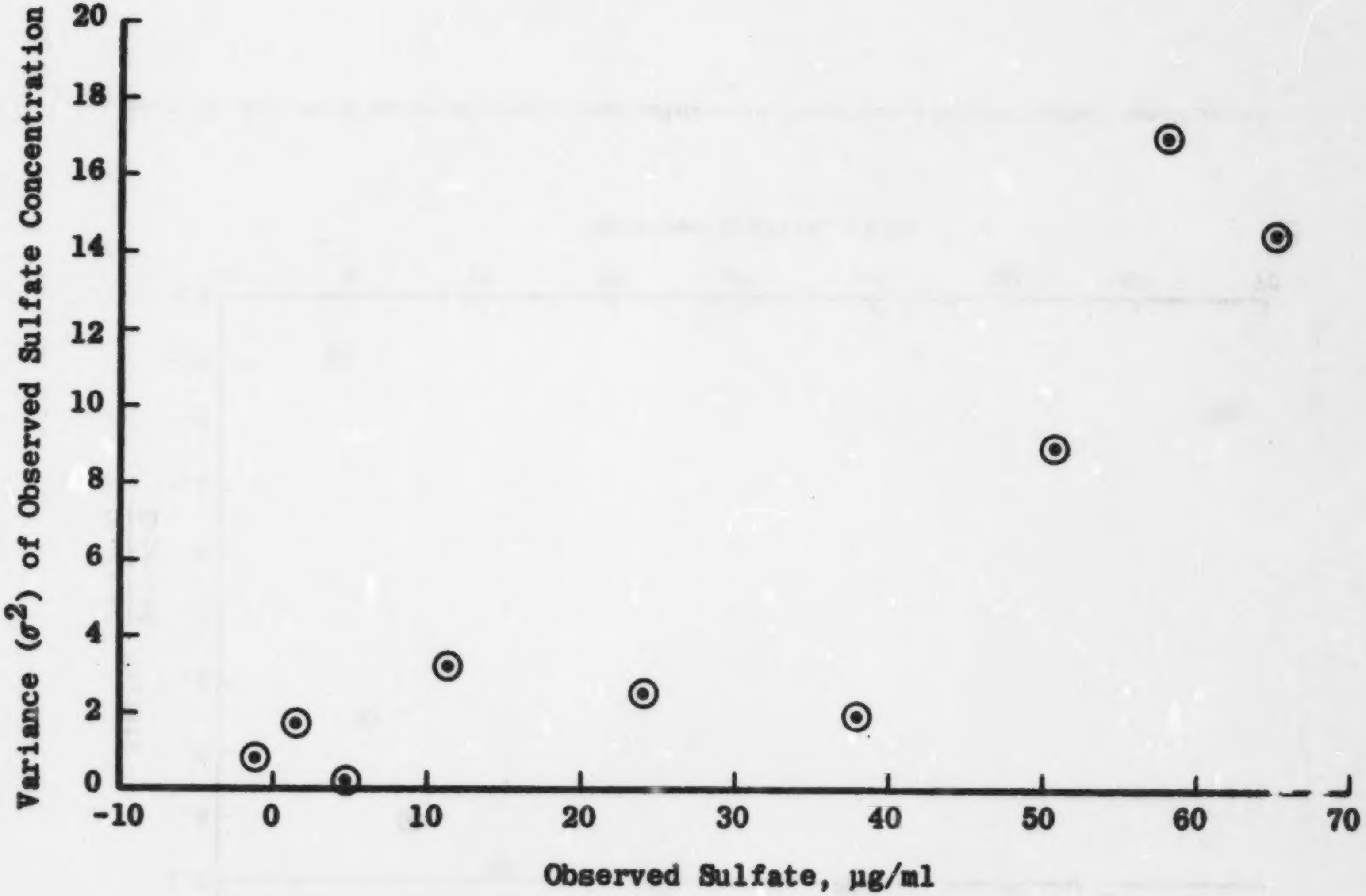


Figure 11. Variance of atmospheric sample extract sulfate analyses versus concentration for the barium chloranilate method.

## VI. THE ANALYSIS OF ATMOSPHERIC SAMPLES

### A. Introduction

Samples were collected by EPA personnel at two sites in the St. Louis area, identified as numbers 106 and 124 in Figure 12.[☆] The filter media and samplers are described in Table 10. The resulting samples permit a comparison of results between the three sulfate methods described above as well as an evaluation of precision with air samples. In addition, the Fluoropore samples were analyzed by x-ray fluorescence (as described in the Appendix) by T. Dzubay of EPA/RTP, thus permitting an additional method comparison. Selected samples were also analyzed for potential interferents in wet chemical sulfate determination. Table 11 summarizes the determinations performed on the field samples. The analytical scheme for the field samples is diagrammed in Figure 13.

This section will emphasize the precision of analytical methods for sulfate with atmospheric samples, the degree of agreement between sulfate methods and the analysis of these samples for potential interferents in sulfate determination.

Discussion of filter media effects on collection of sulfate requires knowledge of the effects of interferents extractable from each filter type. Accordingly, such a discussion will be included following presentation of results of the study of interferents with each sulfate method.

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[☆] Samples from sites 106 and 124 are referred to as "urban" and "rural", respectively.

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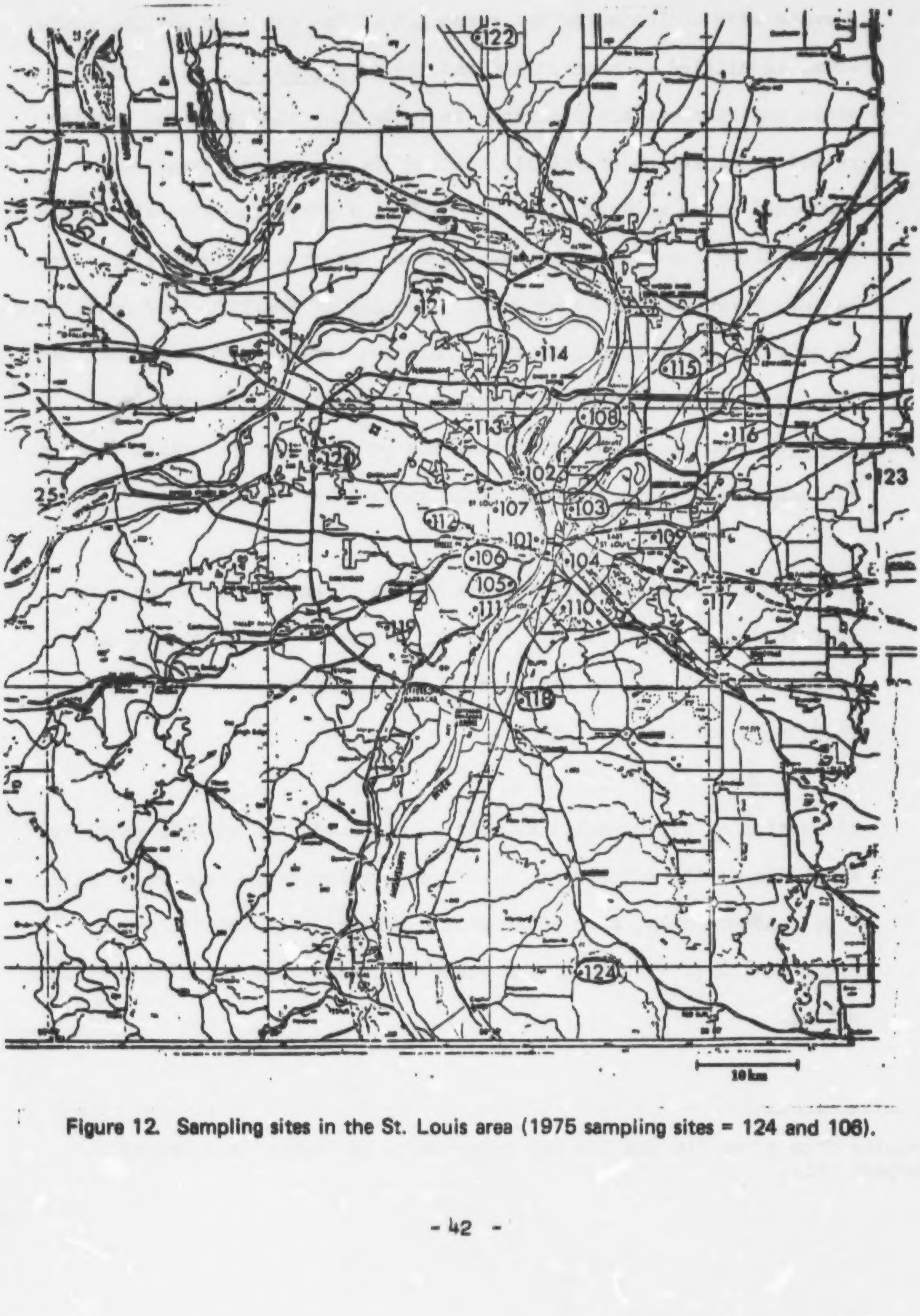
122
121
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108
113
116
120
102
123
25
112
107
103
101
109
106
104
105
111
110
117
119
118
124
10 km

Figure 12. Sampling sites in the St. Louis area (1975 sampling sites = 124 and 106).

## TABLE 10

## SAMPLERS AND FILTER MEDIA EMPLOYED

| Sampler | Size Range, µm | Size Code | Filter Diameter, mm | Flow Rate 1/min | Filter Medium |
|---|---|---|---|---|---|
| Hi-Vol | — | Total | 203 x 254[d] | 1133 | Glass[a] |
| Manual Dichotomous Sampler[e] | 0 - 3.5 | Fine | 37 | 13.7 | Fluoropore[b] |
| | 3.5 - 20 | Coarse | 37 | 14 | Fluoropore |
| | 0 - 20 | Total | 126 | 200 | Glass and Quartz[c] |

[a] Gelman AE glass fiber.

[b] Fluoropore FALP (1 µm pore size).

[c] Gelman AE and tissue quartz 2500 QAO (Pallflex Products) were used in side-by-side samplers.

[d] Commonly referred to as 8 x 10 inch.

[e] Total filters sampled from the same inlet duct as the dichotomous sampler and is described in a paper by R.K. Stevens and T.G. Dzubay, IEEE Transactions on Nuclear Science, Vol. NS-22, No. 2, 849 (1975).

Table 11

ANALYSIS OF FIELD SAMPLES, NUMBERS OF DETERMINATIONS

| Sample | Samples + Blanks | $PO_4^=$ | $SO_3^=$ | $SiO_3^=$ | $Cl^- + Br^-$ | MTB. | Brosset | Barium Chloranilate | XRF [c] |
|---|---|---|---|---|---|---|---|---|---|
| Fluoropore, fine | 24 | 0 | 0 | 0 | 24 | 24 | 24 | 24 | 24 |
| Fluoropore, coarse | 19 | 0 | 0 | 0 | 0 | 0 | 19 | 0 | 19 |
| Total filter, glass | 22 | 22 | 22 | 44 | 44 | 66 | 66 | 26[a] | 0 |
| Total filter quartz | 24 | 14 | 0 | 48 | 14 | 72 | 72 | 38[b] | 0 |
| Hi-vol, glass | 19 | 38 | 0 | 0 | 0 | 57 | 0 | 53 | 0 |
| Total | 108 | 74 | 22 | 92 | 82 | 219 | 181 | 141 | 43 |

[a] Duplicate analyses made on estimated 9 samples (plus 4 blanks) for total of 26 determinations.

[b] Because of insufficient sample, 7 samples were analyzed with 2 determinations. The remainder used 3 determinations.

[c] Analyses by T. Dzubay, EPA/RTP for total sulfur expressed as sulfate. Other elements were also measured.

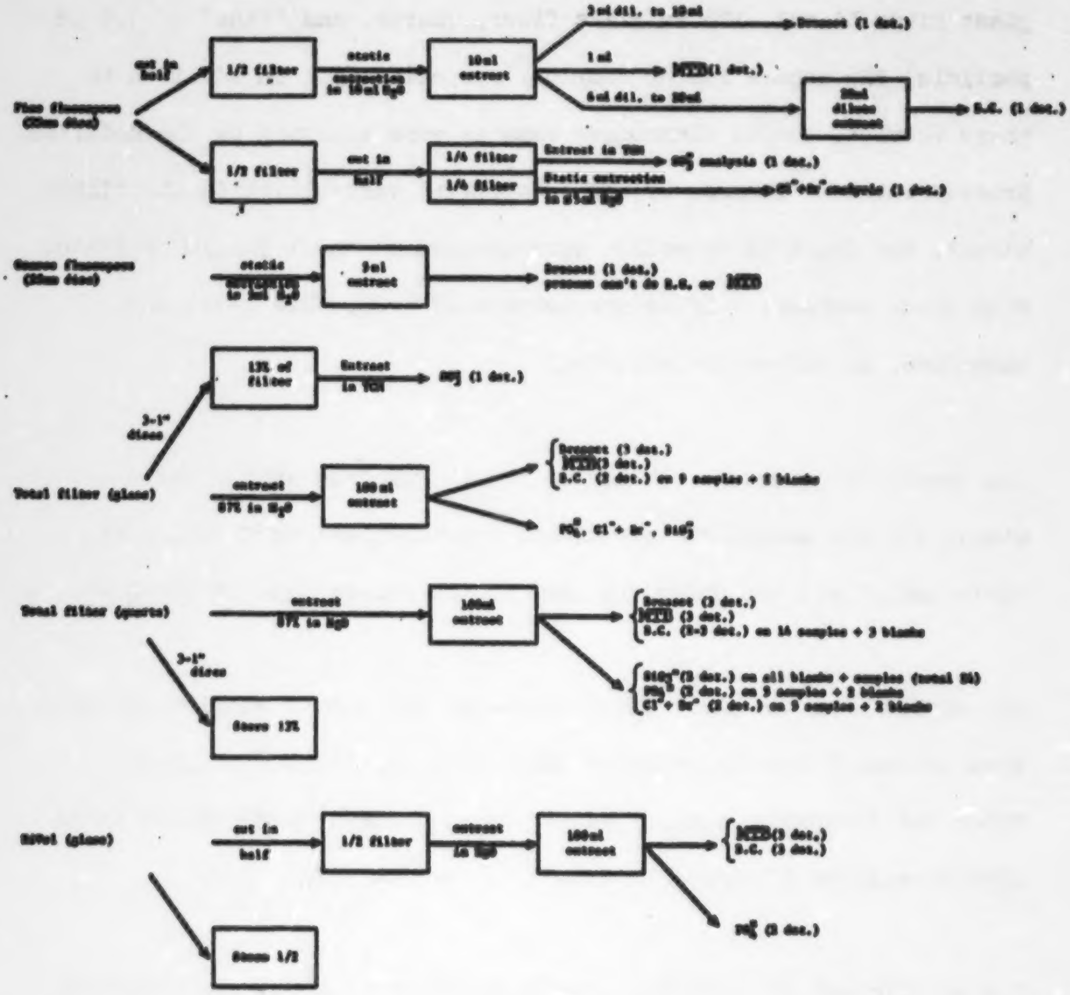

cut in half
1/2 filter
static extraction in 10ml H2O
10ml extract
3ml dil. to 10ml
1 ml
MTB (1 det.)
6ml dil. to 20ml
20ml dilute extract
S.C. (1 det.)
1/2 filter
cut in half
1/4 filter
1/4 filter
Extract in TCN
SO3= analysis (1 det.)
Static extraction in 6ml H2O
Cl- + Br- analysis (1 det.)
static extraction in 3ml H2O
3ml extract
(1 det.)
process can't do S.C. or MTB
13% of filter
Extract in TCN
(1 det.)
3-1" discs
Total filter (glass)
extract 87% in H2O
100 ml extract
(3 det.)
MTB (3 det.)
S.C. (3 det.) on 9 samples + 2 blanks
PO4=, Cl- + Br-, SiO3=
Total filter (quartz)
extract 87% in H2O
100ml extract
(3 det.)
MTB (3 det.)
S.C. (2-3 det.) on 16 samples + 3 blanks
(2 det.) on all blanks + samples
PO4= (2 det.) on 9 samples + 2 blanks
Cl- + Br- (2 det.) on 9 samples + 2 blanks
3-1" discs
Save 13%
HiVol (glass)
cut in half
1/2 filter
extract in H2O
100ml extract
MTB (3 det.)
S.C. (3 det.)
PO4= (3 det.)
Save 1/2

Figure 13. Analytical scheme for atmospheric samples.

## B. Sulfate Analysis of Atmospheric Samples

Tables 12, 13, 14, and 15 present sulfate values obtained with glass fiber hi-vol, 126 mm glass fiber, quartz, and "fine" (< 3.5 µm particle) Fluoropore filter samples, respectively. In addition to these results, coarse Fluoropore samples were analyzed by the modified Brosset method. Because of the substantial variability in the filter blanks, the limit of detection corresponded to ca. 1.5 $\mu g/m^3$ sulfate. With these samples, sulfate was invariably below this level and, therefore, no values are reported.

The degree of agreement between methods, expressed as the ratio of means, and the analytical precision, expressed as coefficients of variation (C.V.) are shown for each filter sample type in Table 16.

The results for the glass fiber hi-volume and quartz samples indicate good agreement between methods while those for the 126 mm glass fiber and Fluoropore samples differ by up to 16%. Such filter media effects will be discussed in detail in Section VIII.

The coefficient of variation of the MTB method was low and relatively constant (1.1-2.4%) and compares to a C.V. of 3% for St. Louis glass fiber hi-vol samples reported in the interim report.[1] The modified Brosset and barium chloranilate methods were less precise (C.V. = 5 to 9%) especially with the 126 mm glass fiber filter samples.

Table 12

SULFATE ANALYSIS OF GELMAN AE 8 X 10" HI-VOL FILTER SAMPLES ($\mu g/m^3$)[a]

| Sample[b] | MTB[c] | Barium Chloranilate[d] |
|---|---|---|
| 0601 GH | 7.0 ± .1 | 7.3 ± .2 |
| 0604 GH | 23.4 ± .7 | 22.8 ± .9 |
| 0605 GH | 13.1 ± .1 | 13.0 ± .4 |
| 0606 GH | 6.8 ± .1 | 6.7 ± .4 |
| 0616 GH | 22.7 ± .3 | 21.6 ± .5 |
| 0618 GH | 12.6 ± .1 | 12.6 ± .5 |
| 0619 GH | 6.1 ± .2 | 6.5 ± .2 |
| 1201 GH | 3.2 ± .1 | 3.5 ± .3 |
| 1202 GH | 3.9 ± .1 | 4.1 ± .3 |
| 1203 GH | 24.6 ± .4 | 22.6 ± .8 |
| 1204 GH | 22.4 ± .6 | 21.6 ± 1.3 |
| 1205 GH | 9.7 ± .1 | 10.2 ± .1 |
| 1206 GH | 4.8 ± .1 | 5.3 ± .2 |
| 1210 GH | 11.1 ± .1 | 11.1 ± .5 |
| 1211 GH | 12.6 ± .1 | 12.9 ± .6 |
| 1212 GH | 4.8 ± .2 | 5.2 ± .2 |
| 1219 GH | 8.3 ± .1 | 9.1 ± .3 |

---

[a] Mean ± 1σ for three determinations.

[b] The first two digits indicate sampler number and the second pair of digits, the sampling day in numerical sequence. "GH" indicates "Glass Hi-Vol". Sampler 06 used at urban site and 12, at rural site.

[c] Filter blank below working range and taken to be zero.

[d] Filter Blank = 296 ± 165 μg/filter (mean of 2) or 0.2 ± .1 $\mu g/m^3$.

## Table 13

## SULFATE ANALYSIS OF 126 mm GELMAN AE GLASS FIBER FILTER SAMPLES ($\mu g/m^3$)[a]

| Sample ID[b] | MTB[c] | Brosset[d] | BC[e)f)] |
|---|---|---|---|
| 0201TG | 8.2 ± .1 | 7.1 ± .6 | 7.0 ± .3 |
| 0202TG | 11.2 ± .1 | 11.9 ± 1.8 | |
| 0203TG | 23.9 ± .1 | 21.3 ± 1.7 | 19.0 ± 1.4 |
| 0204TG | 28.2 ± .2 | 25.5 ± 2.4 | |
| 0205TG | 15.9 ± .2 | 14.5 ± .3 | 12.4 ± 1.5 |
| 0206TG | 7.2 ± .03 | 6.5 ± .3 | 5.4 ± .3 |
| 0219TG | 7.6 ± .04 | 6.9 ± .2 | |
| 0801TG | 3.1 ± .1 | 1.2 ± .1 | |
| 0802TG | 3.9 ± .1 | 2.0 ± .3 | |
| 0803TG | 25.8 ± .2 | 23.1 ± 1.6 | 23.8 ± 1.2 |
| 0804TG | 25.0 ± .3 | 22.0 ± 2.0 | 22.6 ± .4 |
| 0805TG | 10.8 ± .03 | 9.9 ± .2 | 7.9 ± .02 |
| 0806TG | 5.1 ± .1 | 3.8 ± .1 | |
| 0810TG | 13.8 ± .1 | 12.5 ± .4 | |
| 0811TG | 15.7 ± .1 | 14.4 ± .4 | 12.9 ± .5 |
| 0812TG | 5.1 ± .1 | 3.7 ± .3 | |
| 0819TG | 11.2 ± .1 | 9.9 ± .5 | 9.0 ± 1.0 |

---

[a] Values shown are means for three determinations, except as noted, and the standard deviation.

[b] "TG" indicates "glass fiber total filter." Sampler 02 used at urban site and 08, at rural site.

[c] Uncorrected for filter blanks since blanks below the working range.

[d] Corrected for filter blank: 419 ± 194 $\mu g$/126 mm filter or 1.6 ± .8 $\mu g/m^3$
limit of detection: 1.6 $\mu g/m^3$

[e] Corrected for filter blank: 414 ± 111 $\mu g$/filter (mean of 4) or 1.6 ± .4 $\mu g/m^3$
limit of detection: 0.8 $\mu g/m^3$

[f] Mean ± 1$\sigma$ for two determinations.

## Table 14

## SULFATE ANALYSIS OF 126 mm PALLFLEX 2500 QAO QUARTZ FILTER SAMPLES ($\mu g/m^3$)[a]

| Sample ID[b] | MTB[c] | Brosset[f] | BC[d] |
|---|---|---|---|
| 0101TQ | 7.6 ± .3 | 8.0 ± .2 | 11.6 ± .3[e] |
| 0102TQ | 9.7 ± .3 | 10.6 ± .3 | 9.3 ± .6 |
| 0103TQ | 22.3 ± .5 | 23.2 ± 1.0 | 22.2 ± 1.6[e] |
| 0104TQ | 27.4 ± .3 | 27.7 ± .2 | |
| 0105TQ | 14.6 ± .4 | 15.4 ± .4 | |
| 0106TQ | 6.0 ± .1 | 6.3 ± .1 | 5.9 ± .1[e] |
| 0116TQ | 28.1 ± .4 | 29.2 ± .4 | 25.6 ± 1.8 |
| 0118TQ | 14.9 ± .2 | 15.8 ± .2 | 15.1 ± .9 |
| 0119TQ | 6.5 ± .1 | 6.9 ± .3 | |
| 0701TQ | 2.7 ± .1 | 1.5 ± .3 | |
| 0702TQ | 3.7 ± .1 | 3.1 ± .3 | 3.8 ± .3[e] |
| 0703TQ | 24.9 ± .2 | 24.4 ± .7 | |
| 0704TQ | 23.2 ± .2 | 22.5 ± 1.3 | 21.0 ± .5 |
| 0705TQ | 10.1 ± .1 | 10.2 ± .4 | 10.6 ± .5 |
| 0706TQ | 4.5 ± .2 | 3.9 ± .1 | 4.2 ± .4[e] |
| 0710TQ | 10.4 ± .1 | 11.0 ± 1.8 | 9.2 ± .5[e] |
| 0711TQ | 12.1 ± .1 | 11.7 ± .3 | 10.5 ± .5 |
| 0712TQ | 5.1 ± .2 | 4.4 ± .1 | 3.9 ± .8[e] |
| 0719TQ | 8.0 ± .2 | 8.0 ± .1 | 7.2 ± .1 |

---

[a] Values shown are means for three determinations except where noted, and the standard deviation.

[b] TQ indicates "quartz fiber total filter." Sampler 01 used at urban site and 07, at rural site.

[c] Uncorrected for filter blank since blanks below working range.

[d] Corrected for filter blank: 131 ± 191 μg/filter (mean of 3) or 0.5 ± .7 $\mu g/m^3$

[e] Two trials

[f] Corrected for filter blank: 144 ± 45 μg/filter or 0.6 ± .2 $\mu g/m^3$. Limit of detection: 0.4 $\mu g/m^3$.

## Table 15

## SULFATE ANALYSES OF "FINE" FLUOROPORE FALP FILTER SAMPLES (μg/m$^3$)[a]

| Sample ID[b] | MTB[c] | Brosset[d] | BC[e] | XRF S as Sulfate |
|---|---|---|---|---|
| 301FF | (7.8) | 3.8 | 5.1 | 4.9 |
| 302FF | 9.7 | 8.3 | 8.2 | 9.6 |
| 303FF | 20.6 | 20.2 | 11.9 | 18.7 |
| 304FF | 24.8 | 26.4 | 23.9 | 24.6 |
| 305FF | 14.2 | 13.5 | 5.6 | 13.9 |
| 306FF | (7.9) | 4.5 | < 4.8 | 6.4 |
| 316FF | 28.5 | 30.3 | 27.4 | 24.0 |
| 318FF | 13.5 | 11.9 | 14.8 | 14.1 |
| 319FF | (7.8) | 4.9 | 5.7 | 6.5 |
| 419FF | 8.3 | 4.6 | < 4.8 | 6.5 |
| 901FF | (ca. 0) | < 1.6 | < 5.1 | --[f] |
| 902FF | (7.2) | 2.6 | < 4.8 | 3.6 |
| 903FF | 25.5 | 25.4 | 25.1 | 20.9 |
| 904FF | 23.0 | 22.8 | 18.7 | 22.1 |
| 905FF | 11.1 | 8.8 | 5.8 | 9.4 |
| 906FF | (7.2) | 3.5 | < 4.6 | 4.6 |
| 910FF | 12.0 | 9.5 | < 4.8 | 10.6 |
| 911FF | 12.6 | 10.9 | 10.2 | 11.7 |
| 912FF | (7.6) | 3.4 | < 4.7 | 4.6 |
| 919FF | 9.9 | 6.9 | 15.6 | 7.6 |

---

a. Results for single trials because of insufficient sample.

b. FF indicates fine Fluoropore filters.

c. Values shown in parentheses result from sulfate readings below 6 μg/ml and are probably too high. Filter blanks were below 6 μg/ml and taken to be zero.

$$\mu g/m^3 = \frac{\mu g/\text{filter}}{\text{vol } (m^3)} \quad \text{where vol}(m^3) = \frac{0.98 \times \text{time (min.)} \times \text{flow (l/min)}}{1000}$$

d. Corrected for filter blank: 24.9 ± 23.4 μg/37 mm filter (mean of 6)
Limit of detection: 47 μg/37 mm filter (1.5 μg/m$^3$)

e. Corrected for filter blank: 97.0 ± 45.4 μg/37 mm filter (mean of 4)
Limit of detection: 91 μg/37 mm filter (4.8 μg/m$^3$)

f. No value reported.

## Table 16

## PRECISION AND METHOD COMPARISONS WITH ATMOSPHERIC SAMPLES
(Relative to the MTB Method)

| Filter | MTB[a] | | Brosset[a] | | BC[a] | | XRF |
|---|---|---|---|---|---|---|---|
| | Rel. Results | C.V. (%) | Rel. Results | C.V. (%) | Rel. Results | C.V. (%) | Rel. Results |
| Hi-vol (glass) | 1.0 | 2.4 | N.D.[b] | - | 1.0 ± .01 | 4.6 | N.D. |
| 126 mm glass | 1.0 | 1.1 | 0.89 ± .02 | 9.3 | .84 ± .02 | 6.7 | N.D. |
| 126 mm quartz | 1.0 | 1.8 | 1.0 ± .01 | 4.7 | .97 ± .02 | 6.8 | N.D. |
| Fluoropore (fine) | 1.0[e] | -[c] | 0.93[e] | -[c] | .87[e] | -[c] | .91[d] |

a. Values shown are ratios of means excluding values below the working ranges. Coefficients of variations pooled for each filter type.

b. Not determined.

c. Since only single determinations were possible, precision not obtainable.

d. Results obtained with both linear and third order regression of MTB data.

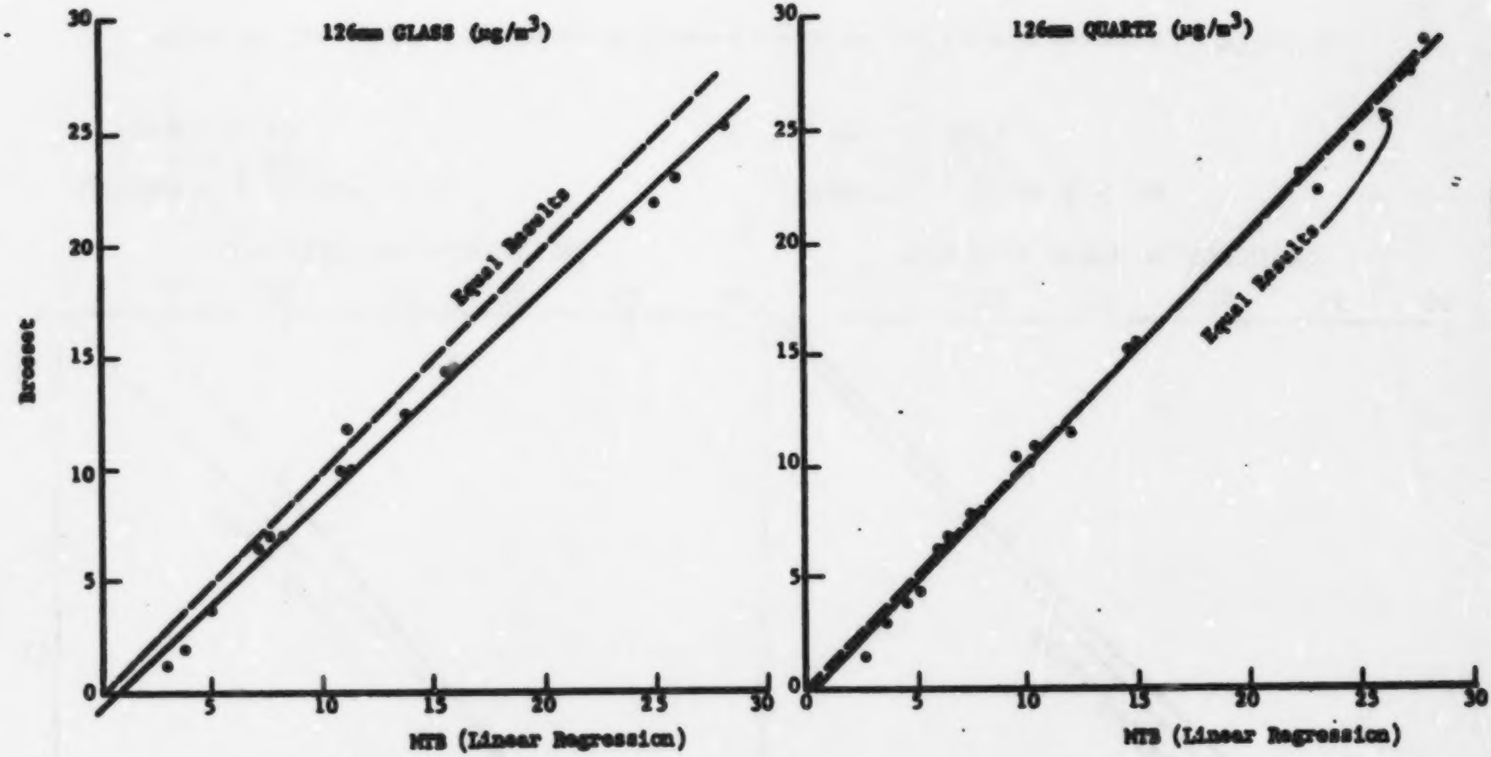
A more detailed comparison of methods is given in Figures 14-18 which plot results by filter type for MTB vs. Brosset, Brosset and MTB vs. XRF and MTB vs. the BC method. With one exception, results are highly correlated ($r > 0.98$). The poorest correlation was found with the MTB-BC comparison for fine Fluoropore samples. This is thought to reflect primarily the imprecision of the BC method for low level sulfate samples.

For Fluoropore samples which provided sulfate levels near the bottom of the MTB methods working range the results by that technique varied significantly depending on the procedure used for fitting the working curve. Figure 15 illustrates the substantial improvement in agreement between the MTB and Brosset techniques for these samples using a third order polynomial fit rather than linear regression. With the other samples the choice of curve fitting procedures had minimal impact. Comparing XRF and wet chemical results by the Brosset and MTB methods (third order regression), XRF results are consistently lower at high concentrations.

A general comparison of results between the first and second year's program is complicated by the use of different methods, a different version of the Brosset technique and different sampling techniques. Table 17 lists the feasible comparison. Brosset results for the current program reflect somewhat better agreement with the MTB method.

## C. The Analysis of Atmospheric Samples for Potential Interferents

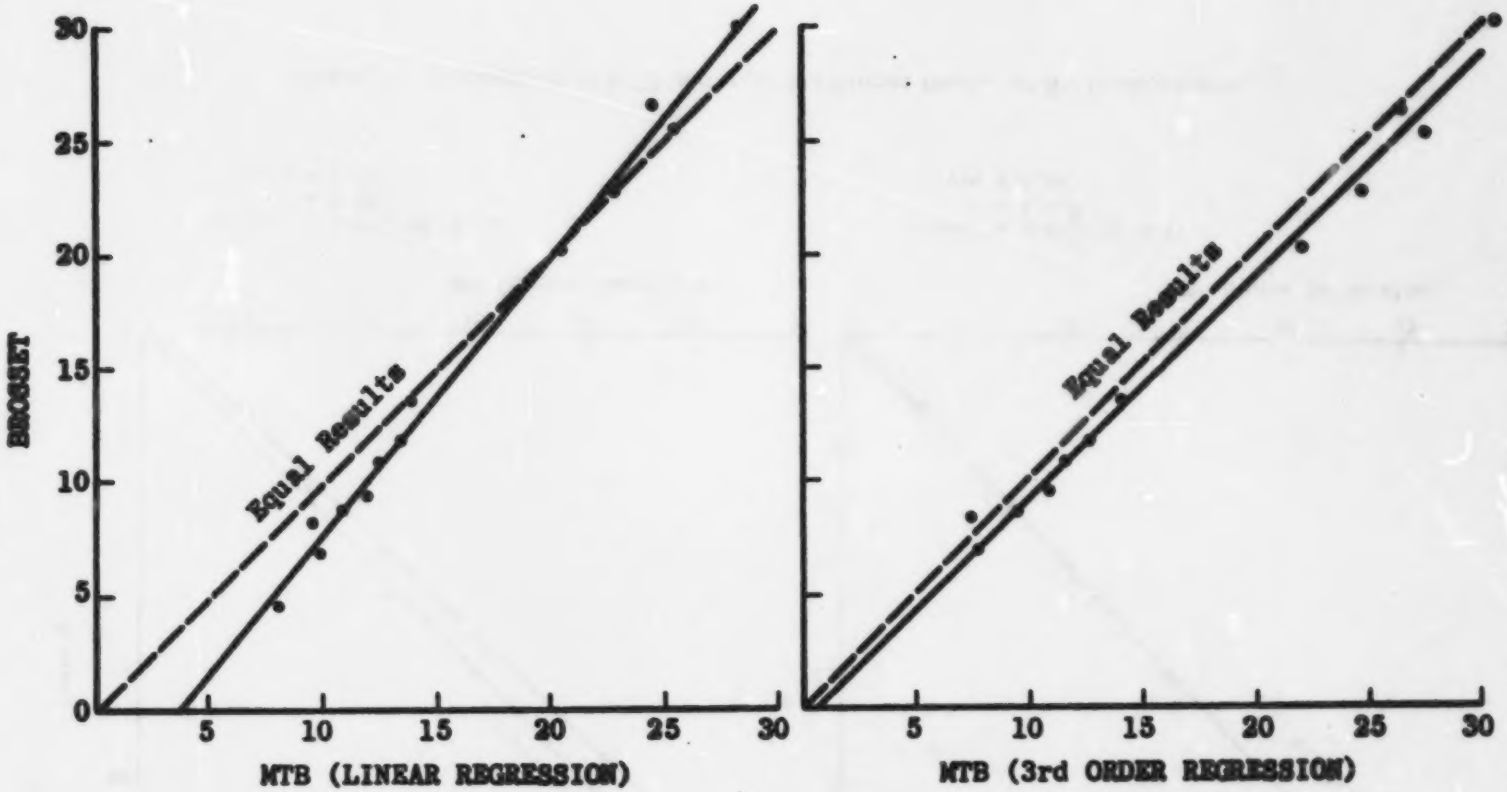
Previous studies, reported in the Interim Report for this contract, have demonstrated that ions such as silicate, phosphate, halogen and sulfite can interfere in various wet chemical sulfate methods.[1] The significance of these observations remains unclear until the concentrations of these species in real sample extracts are determined. The present study provided for such determinations on selected



Brosset = 0.93 [MTB] -0.61
r = 0.996
Sy·x = 0.75

Brosset = 1.03 [MTB] -0.27
r = 0.997
Sy·x = 0.66

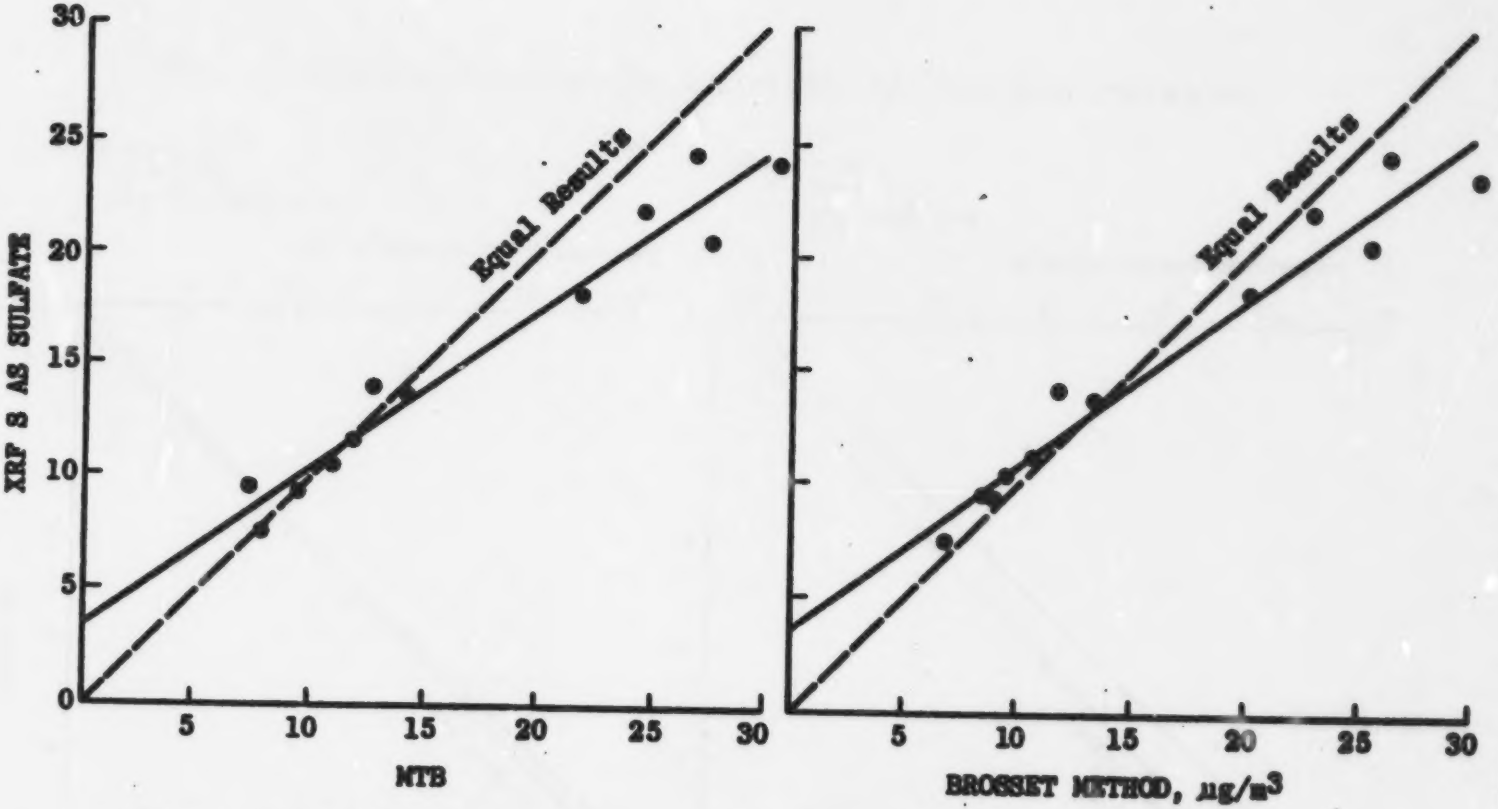
Figure 14. Comparison of MTB and modified Brosset results for St. Louis samples.



BROSSET = 1.21 [MTB] -4.62
r = 0.997
Sy·x = 0.70

BROSSET = 0.97 [MTB] -0.49
r = 0.996
Sy·x = 0.77

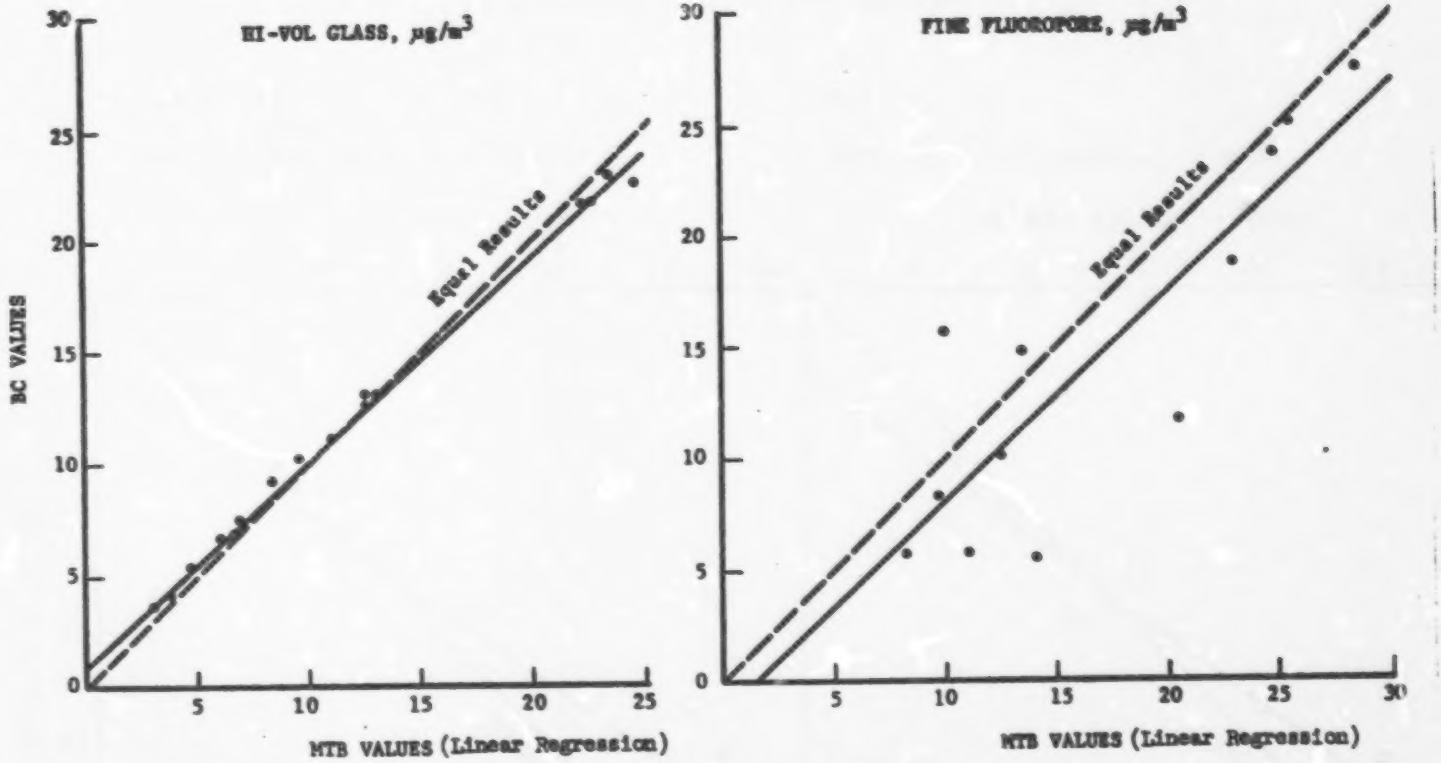
Figure 15. Comparison of Brosset and MTB results using linear and 3rd order regression for MTB data.



XRF = 0.710 [MTB] + 3.37
r = 0.978
Sy•x = 1.35

XRF = 0.730 [BROSSET] + 3.74
r = 0.981
Sy•x = 1.26

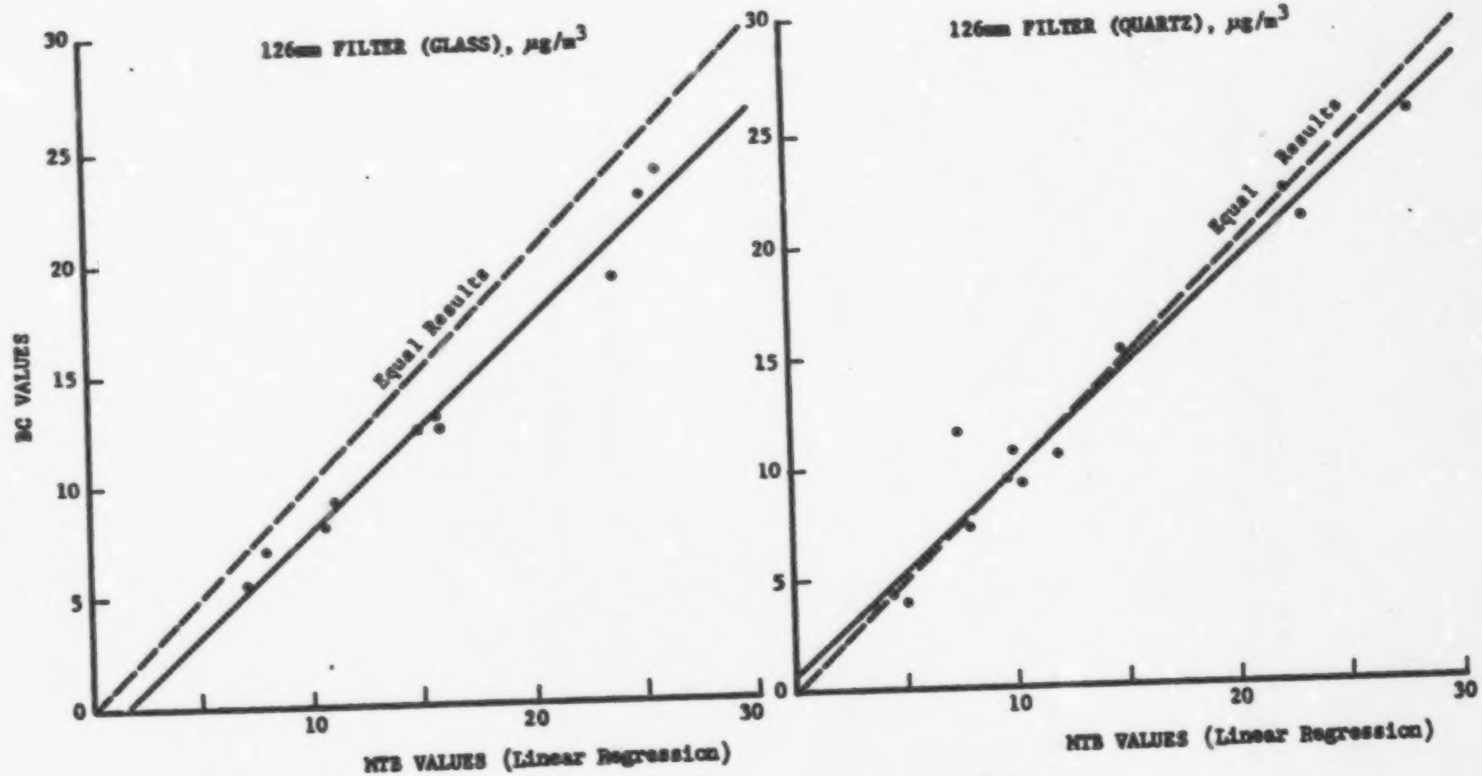
Figure 16. Comparison of XRF, MTB (3rd order regression), and Brosset results.



$BC = 0.92[MTB] + 0.89$
$r = 0.999$
$S_{y \cdot x} = 0.38$

$BC = 0.95[MTB] - 1.49$
$r = 0.86$
$S_{y \cdot x} = 4.19$

Figure 17. Comparison of barium chloranilate (BC) and MTB sulfate values for St. Louis samples.



$BC = 0.93\,[MTB] - 1.56$
$r = 0.99$
$Sy \cdot x = 1.03$

$BC = 0.91\,[MTB] + 0.68$
$r = 0.98$
$Sy \cdot x = 1.45$

Figure 18. Comparison of barium chloranilate (BC) and MTB sulfate values for St. Louis samples.

## Table 17

## COMPARISON OF RELATIVE SULFATE RESULTS IN THE FIRST AND SECOND YEARS OF THIS STUDY WITH ST. LOUIS SAMPLES

| Sample | MTB | Brosset | XRF[a] |
|---|---|---|---|
| | | 1974 | |
| Fluoropore, "fine" | 1.0 | 1.15 | 0.93 |
| Glass fiber[b] | 1.0 | 0.76 | --- |
| | | 1975 | |
| Fluoropore, "fine" | 1.0 | 0.93 | 0.91 |
| Glass fiber[c] | 1.0 | 0.89 | --- |

---

a. Data of T. Dzubay, EPA/RTP.

b. 37 mm Gelman AA glass fiber filters (Batch 8188) at 12 lpm.

c. 126 mm Gelman AE glass fiber filters at 200 lpm.

interferents for samples collected at urban and rural sites in the St. Louis area. Aqueous extracts were analyzed for silicate, phosphate, halide (primarily chloride), turbidity and "yellowness" (e.g. absorbance at 420 nm) and filter sections were analyzed for sulfite.

It was recognized that in some cases the filter medium would be the dominant source of the interferent. In such instances, a measurement of ambient concentrations would probably not be feasible. However, the important parameter to be obtained was the gross extract concentration of the interferent from all sources. Since such concentrations depend on the size of the filter section extracted and the extract volume, observed concentrations were adjusted to correspond to an EPA extraction protocol for hi-vol filter sections in designing the interferent study (Section VI, A).

### 1. Silicate Analysis*

The 126 mm glass and quartz filters, less 3 - 1" discs were extracted into a final volume of 100 ml. These aqueous extracts were analyzed for silicate using the technique detailed in Appendix F. This procedure measures "reactive silicate" by which is meant those soluble silicate species which react with molybdic acid. This restricts the determination to monomeric and/or dimeric silicates. Since silicates depolymerize at high pH, the results can be expected to be pH-dependent to some degree.

---

*It should be noted that these results relate only to the water-soluble portion of the total silicate in the sample and filter medium. No relationship is expected between these results and soil levels in the particulate samples.

Table 18 lists results, expressed as $\mu g/m^3$, for both filter types. The results for glass fiber are all below detectable limits because of a high blank. The samples in all cases yielded silicate values less than those of the mean blank value. It is concluded that the glass fiber filter itself is the source of most of the silicate in the extract and that the contribution of silicate from the particulate sample is relatively small.

For the tissue quartz filter samples, the blank values are low and measurable atmospheric silicate levels were obtained in some cases. Silicate levels from the rural site were generally below detection.

### 2. Phosphate Analysis

Phosphate analyses were done by the molybdenum blue method as detailed in Appendix G. Analyses of glass fiber filters were done with one trial because of insufficient sample. The results given in Table 19 indicate low but measurable atmospheric values in all cases. Results for selected tissue quartz samples are also given. The calculated atmospheric concentrations from samples collected on quartz are about a factor of 10 lower than

## Table 18

## SILICATE ANALYSES OF AQUEOUS EXTRACTS FROM 126 mm GLASS AND QUARTZ FIBER TOTAL FILTER SAMPLES[a]

| Glass Fiber | | Quartz Fiber | |
|---|---|---|---|
| Sample ID | Silicate (as $SiO_2$) $\mu g/m^3$[b] | Sample ID | Silicate (as $SiO_2$) $\mu g/m^3$[c] |
| 201TG | < 1.1 | 101TQ | 5.1 |
| 202TG | < 1.1 | 102TQ | 14.3 |
| 203TG | < 1.1 | 103TQ | 4.1 |
| 204TG | < 1.1 | 104TQ | 1.8 |
| 205TG | < 1.1 | 105TQ | 1.9 |
| 206TG | < 1.1 | 106TQ | 2.6 |
| 219TG | < 1.1 | 116TQ | < 1.2 |
| | | 118TQ | 4.4 |
| | | 119TQ | 9.8 |
| 801TG | < 1.1 | 701TQ | 2.0 |
| 802TG | < 1.1 | 702TQ | < 1.2 |
| 803TG | < 1.1 | 703TQ | < 1.2 |
| 804TG | < 1.1 | 704TQ | < 1.2 |
| 805TG | < 1.1 | 705TQ | < 1.2 |
| 806TG | < 1.1 | 706TQ | < 1.2 |
| 810TG | < 1.1 | 710TQ | < 1.2 |
| 811TG | < 1.1 | 711TQ | < 1.2 |
| 819TG | < 1.1 | 712TQ | < 1.2 |
| | | 719TQ | < 1.2 |

| Glass Fiber | Quartz Fiber |
|---|---|
| Mean Blank = 84.0 ± 1.3 μg/ml | Mean Blank = 5.2 ± 1.5 μg/ml |
| or 9655 ± 149 μg/filter | or 598 ± 172 μg/filter |

---

a. Total filter area 109.5 $cm^2$ (88% of 126 mm filter) extracted with final volume 100 ml.

b. The gross μg/ml silicate were, in all cases, less than the value for the filter blank.

c. Results are calculated for the second of two trials. The first trial was rejected because of experimental difficulties.

## TABLE 19

## PHOSPHATE ANALYSES OF 126 mm GLASS AND QUARTZ FIBER FILTER SAMPLES[a]

| Glass Fiber[b] | | | Quartz Fiber[c] | | |
|---|---|---|---|---|---|
| Sample ID | $PO_4^{\equiv}$ (μg/ml)[d] | $PO_4^{\equiv}$ ($\mu g/m^3$)[d] | Sample ID | $PO_4^{\equiv}$ (μg/ml)[d] | $PO_4^{\equiv}$ ($\mu g/m^3$)[d] |
| 201TG | .35 | 0.15 | | | |
| 202TG | .41 | 0.17 | | | |
| 203TG | .47 | 0.20 | | | |
| 204TG | .31 | 0.13 | 104TQ | .03 | .01 |
| 205TG | .33 | 0.14 | 105TQ | .03 | .01 |
| 206TG | .09 | 0.04 | | | |
| 219TG | .03 | 0.01 | 119TQ | .00 | < .005 |
| 801TG | .10 | 0.04 | 701TQ | - .01 | < .005 |
| 802TG | .20 | 0.09 | | | |
| 803TG | .16 | 0.07 | 703TQ | - .01 | < .004 |
| 804TG | .19 | 0.08 | | | |
| 805TG | .10 | 0.04 | | | |
| 806TG | .17 | 0.07 | | | |
| 810TG | .16 | 0.07 | | | |
| 811TG | .40 | 0.17 | | | |
| 812TG | .30 | 0.12 | | | |
| 819TG | .17 | 0.07 | | | |

Mean Blank = –.02 ± .01 μg/ml     Mean Blank = .01 ± .005 μg/ml those obtained on glass fiber. The cause of the higher apparent atmospheric phosphate levels from glass fiber filter samples is unclear. The atmospheric concentrations observed on quartz filters are considered more reliable.

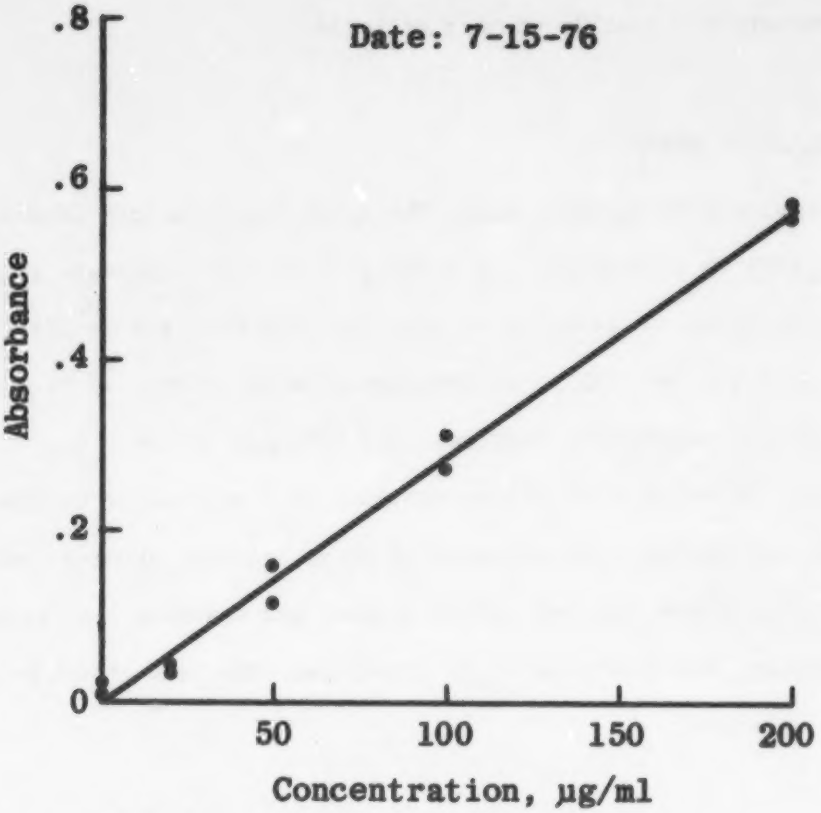
---

[a] See footnote a, Table 18.
[b] Sample sufficient for only one determination.
[c] Corrected for filter blank.
[d] Mean of two trials.

### 3. Chloride Analysis

Samples were analyzed using the $AgNO_3$ turbidimetric method.[2] Figure 19 illustrates the working curve with duplicate standards. This technique responds to chloride, bromide, and iodide and is subject to several other interferences not likely to be significant in atmospheric samples. The intended strategy was to employ XRF Br values from filter analyses as a measure of bromide ions in the extract. By subtracting these from the apparent chloride (after correction for atomic weight) and assuming negligible iodide, the remainder would approximate the true chloride concentration.

Tables 20 and 21 list results for observed halide ion (as chloride) on glass and quartz filters, respectively. In both cases, the relatively high and variable filter blanks resulted in atmospheric concentrations below detectable limits. Table 20 also lists XRF bromine values which are 2 or 3 orders of magnitude below the detectable limit for chloride by the turbidimetric method for these samples.



Date: 7-15-76

ABS = .002 + .003 [Conc.]
Sy•x = .0191

Figure 19. Chloride calibration curve.

## TABLE 20

## HALIDE (AS CHLORIDE) ANALYSIS OF 126 mm GLASS FIBER FILTER SAMPLES

| Sample ID | Observed $Cl^-$, μg/ml[a] | $Cl^-$, μg/$m^3$ | Br, μg/$m^3$[b] |
|---|---|---|---|
| 202TG | 14.8 | < 10.9 | .057 |
| 204TG | 6.1 | < 10.9 | .042 |
| 219TG | 9.3 | < 10.6 | .150 |
| 801TG | 21.4 | < 10.5 | - |
| 802TG | 31.2 | < 11.1 | .012 |
| 803TG | 5.1 | < 10.3 | .008 |
| 804TG | 4.0 | < 10.5 | .012 |
| 806TG | 17.3 | < 10.6 | .006 |
| 810TG | 7.2 | < 11.1 | .010 |
| 812TG | 14.5 | < 10.3 | .016 |

Filter Blank: 21.8 ± 12.7 μg/ml
or 2500 ± 1450 μg/filter

a. Not corrected for filter blank.

b. By XRF of the fine particle fraction on Fluoropore filters collected by the dichotomous sampler.

## TABLE 21

## HALIDE (AS CHLORIDE) ANALYSIS OF 126 mm QUARTZ FIBER FILTER SAMPLES[a]

| Sample ID | Observed $Cl^-$, $\mu g/ml$[b] | Observed $Cl^-$, $\mu g/m^3$ |
|---|---|---|
| 104TQ | 2.2 | < 2.8 |
| 105TQ | 5.4 | < 2.8 |
| 119TQ | 5.0 | < 2.8 |
| 701TQ | 5.3 | < 2.7 |
| 703TQ | 3.8 | < 2.7 |

Filter Blank: 0.11 ± 3.2 $\mu g/ml$ (mean of 3)
or 12.3 ± 371 $\mu g$/126 mm filter.

a. Mean of two trials.

b. Not corrected for blank.

For the purpose of estimating upper limits to interferent levels for St. Louis samples, the chloride levels, in μg/ml, will be used uncorrected for filter blanks.

The unused halves of the one-inch discs from the fine Fluoropore samples (20 samples and 4 blanks) were extracted in 10 ml $H_2O$ and analyzed for chloride. Results for samples, filter blanks and reagent blanks were not significantly different. Therefore, the data were not reduced.

## 4. Sulfite Analysis

Sections cut from the exposed 126 mm Gelman AE glass fiber filters were extracted in tetrachloromercurate solution and analyzed by the West-Gaeke procedure. The extraction and analytical procedures are detailed in Appendix H. The quantity of sample proved to be sufficient for only a single trial. The results are summarized in Table 22. Also shown is the sulfite expressed as a fraction of the water soluble sulfate for the same glass fiber sample. The latter probably includes both sulfate and sulfite since oxidation of $SO_3^=$ in solution appears to be rapid (at least using synthetic solutions).[1]

The filter samples had been stored at -10°C for about 6 months preceding analyses without protection from oxygen. Therefore, any sulfite surviving on the filter probably exists as a metal-sulfite complex or salt stabilizing the S (IV) from oxidation.

## TABLE 22

## SULFITE ANALYSES OF 126 mm GLASS FIBER FILTER SAMPLES[a]

| Sample ID | $SO_3^=$, μg/ml[b] | $SO_3^=$, μg/m$^3$[b] | $SO_3^=/SO_4^=$, %[c] |
|---|---|---|---|
| 201TG | 0.068 | 0.038 | 0.50 |
| 202TG | 0.042 | 0.023 | 0.21 |
| 203TG | 0.017 | 0.010 | 0.04 |
| 204TG | 0.005 | 0.003 | 0.01 |
| 205TG | < 0.004 | < 0.002 | < 0.01 |
| 206TG | < 0.004 | < 0.002 | < 0.03 |
| 219TG | 0.005 | 0.003 | 0.04 |
| 801TG | 0.089 | 0.05 | 1.6 |
| 802TG | < 0.004 | < 0.002 | < 0.05 |
| 803TG | < 0.004 | < 0.002 | < 0.01 |
| 804TG | < 0.004 | < 0.002 | < 0.01 |
| 805TG | < 0.004 | < 0.002 | < 0.02 |
| 806TG | < 0.004 | < 0.002 | < 0.04 |
| 810TG | 0.004 | 0.002 | 0.01 |
| 811TG | < 0.004 | < 0.002 | < 0.01 |
| 812TG | 0.028 | 0.015 | .29 |
| 819TG | 0.013 | 0.007 | .06 |

Filter Blank: - 0.002 ± .003 μg/ml (mean of 5)
or .3 ± .5 μg/126 mm filter.

Limit of Detection: .0023 μg/ml[d].

[a] Analysis of 15.2 cm$^2$ of filter area extracted into tetrachloromercurate solution. Total volume: 20 ml.

[b] Corrected for blank.

[c] Sulfate values by the MTB method.

[d] Basis twice the σ of the intercept of the working curve.

Accordingly, it is reasonable to seek correlations between sulfite levels and metals which might serve to stabilize sulfite.

It has been suggested[3] that zinc may be involved in fixation of $SO_2$ with the result being zinc sulfite. Accordingly, sulfite levels were examined for possible correlations with XRF Zn values determined by T. Dzubay. Figure 20 shows a scatter diagram of Zn and $SO_3^=$ for the cases where measurable data are available for the same location and date. No correlation is evident.

## 5. Turbidity

Since colloidal particles can remain in suspension in spite of filtration of aqueous extracts, the resulting light scattering can interfere in some sulfate determinations, especially the $BaCl_2$ turbidimetric procedure.[1] Other, more subtle, phenomena (e.g. nucleation of $BaSO_4$ precipitation) may also lead to interference in sulfate measurements.

Although not a part of the initial study design, a limited effort was undertaken to estimate the maximum turbidity to be expected in aqueous extracts. For this purpose, 3/4" x 8" strips were cut from the Gelman AE hi-vol filter samples and extracted following the EPA/EMSL methylthymol blue Technicon II procedure which includes vacuum filtration with a fine porosity fritted disc. Two urban and two rural samples were chosen; the samples used had the

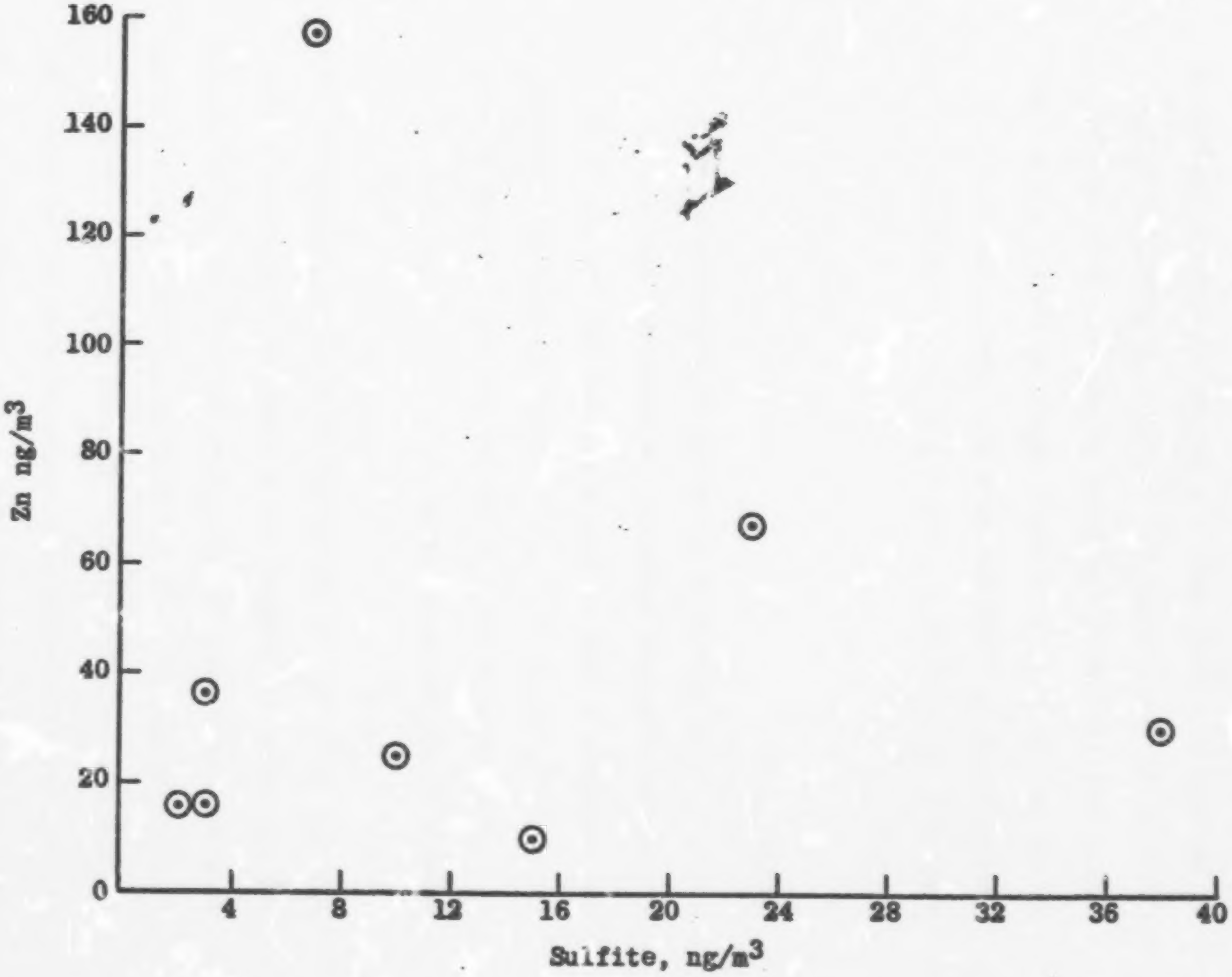


Figure 20. Scatter diagram of zinc versus sulfite concentrations.

two highest sulfate levels experienced at each location. Colloidal clay was selected as a convenient and plausible model for the suspended particles in the extracts. Colloidal solutions were prepared by shaking a portion of bentonite clay in water, allowing the suspension to settle for three hours and filtering through a Whatman No. 1 filter. Ninety degree light scattering was measured at 600 nm using an Aminco Spectrofluorimeter calibrated using the bentonite clay suspensions. The wavelength 600 nm was chosen to avoid fluorescence observed in atmospheric sample extracts at shorter wavelengths. It should be noted that the relationship between clay concentration and light scattering depends on the particle size distribution and may vary with the age of the suspension, between suspensions prepared at different times or with use of different types of clay.

Table 23 summarizes the results expressed as μg/ml clay. These determinations indicate that 40 μg/ml clay approximates the highest level of light scattering particles observed.

### 6. Yellow Chromophore Concentration of Particulate Extracts

Aqueous extracts of atmospheric samples can be decidedly yellow. This corresponds to absorbance in the 400-500 nm region. Since the MTB method employs 460 nm for quantitation some interference would be expected if no blank correction is made.

## TABLE 23

## TURBIDITY OF AQUEOUS EXTRACTS (AS μg/ml COLLOIDAL CLAY OF 8 x 10 GLASS FIBER HI-VOL SAMPLES FROM ST. LOUIS[a])

| Sample ID | Colloidal Clay (μg/ml) |
|---|---|
| 604 GH | 28 |
| 616 GH | 36 |
| 1203 GH | 15.4 |
| 1204 GH | 22 |

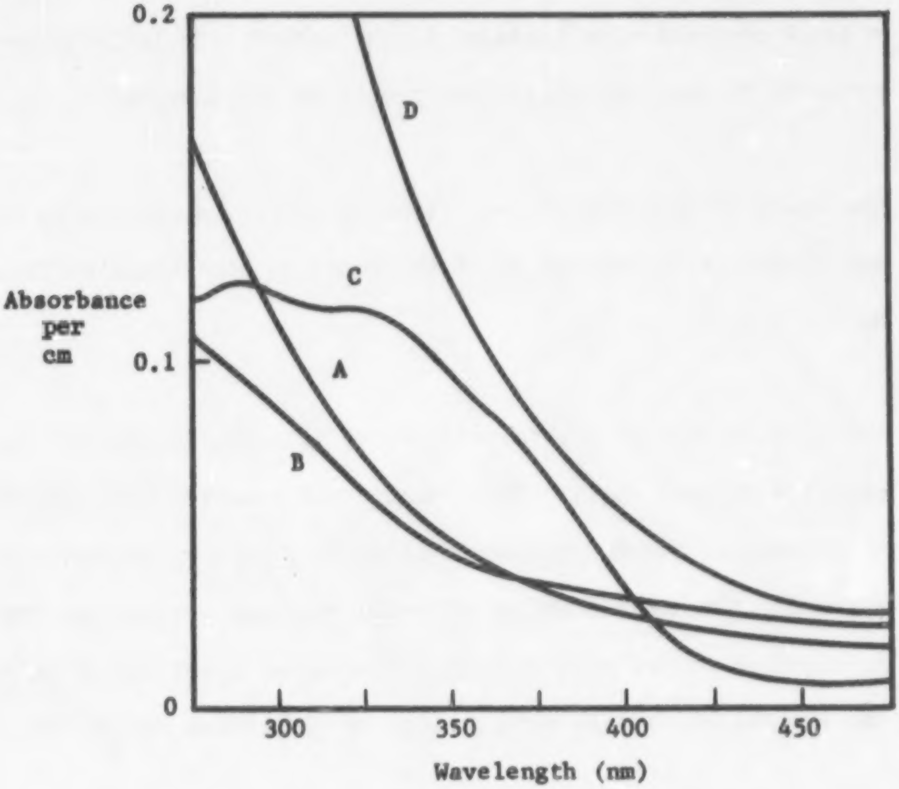
Filter Blank: 10 ± 1 (mean of 2).

[a] A 3/4" x 8" strip extracted by the EMSL/MTB procedure with final volume 50 ml.

Extracts absorbing in the 400-500 nm region will typically absorb even more strongly in the UV region in the vicinity of 312 nm, the wavelength used for quantitation with the BC method. While a blank correction is included in the method, its large value is expected to diminish analytical precision for sulfate.

The study of this interferent required, first, a model chromophore and second, a determination of the relevant concentration for such a model.

UV-Visible scans were obtained for the four St. Louis extracts analyzed for turbidity. The scan for the solution with greatest absorbance in the 400-500 nm is shown in Figure 21 compared to scans for two concentrations of p-benzoquinone (p-bzq) and for a solution of coffee bean extract. Five µg/ml p-bzq approximates the absorbance of this extract both at 312 nm and at 560 nm.



A = 3/4" strip of #616 extracted in 50ml
(most yellow sample)

B = Blank filter extract + 5 μg/ml p-benzoquinone

C = Blank filter extract + 20 μg/ml freeze-dried coffee

D = 15 μg/ml p-benzoquinone in water

Figure 21. Comparison of UV-visible scans of atmospheric sample aqueous extracts and candidate model chromophores.

## VII. EFFECTS OF INTERFERENTS

### A. Study Design

In the first year of this program, interferent concentrations used were 10 and 30 μg/ml with 20 and 60 μg/ml sulfate. This year's concentrations were to be dictated based upon the "highest observed concentrations". However, the observed concentrations, in μg/ml, depend upon the filter size, type, sampled air volume, filter area extracted, and final volume of extract.

Since glass fiber filters, themselves, proved to be a significant source of interferents, the EPA protocol for hi-vol sampling was adopted in calculating the interferent concentrations for this study. The conditions assumed were 24-hour sampling (2000 $m^3$ of air) through an 8 x 10" filter and extraction of a 3/4" x 8" strip into a final volume of 50 ml $H_2O$. It was further assumed that the interferents extracted per unit area from the 126 mm glass fiber and 8 x 10" glass fiber filters were equal. The interferent concentrations observed with the glass fiber 126 mm total filters (which were always greater than those from the tissue quartz filters, loaded or unloaded) were used to calculate concentrations expected under the above-assumed conditions. Although studies of single interferents would be restricted to 5 substances and, for studies with interferent pairs and quartets, to only 4, Table 24 calculates the maximum concentrations expected for 7 potential interferents as determined with atmospheric samples. The variation with analytical method results from the dilution required for analysis by the modified Brosset method.

## Table 24

## CALCULATED MAXIMUM CONCENTRATIONS OF POTENTIAL INTERFERENTS UNDER CONDITIONS SIMULATING EPA PROCEDURES[a]

(μg/ml)

| | METHOD | | |
|---|---|---|---|
| **Species** | **MTB** | **Brosset**[b] | **BC** |
| $PO_4^{\equiv}$ | 0.6 | 0.15 | 0.6 |
| $SiO_3^{=}$ | 60 | 15 | 60 |
| $SO_3^{=}$ | 0.1 | 0.025 | 0.1 |
| $Cl^-$ | 20 | 5 | 20 |
| $Br^-$ | 0.5 | 0.1 | 0.5 |
| Colloidal clay | 40 | 10 | 40 |
| p-benzoquinone[c] | 6[d] | 1.5 | 6 |

a. Extracting a 3/4 x 8" strip from a 24-hour hi-vol sample collected on an 8 x 10" glass fiber filter.

b. Concentrations are 1/4 of the values calculated for the MTB and BC methods based on the need for an approximately four-fold dilution into the working range of the Brosset Method.

c. A model yellow chromophore.

d. 6 μg/ml used instead of 5 for experimental convenience.

Excepting for phosphate, these concentrations served as the basis for interference studies. The phosphate concentration was increased by a factor of ca. 20 at the request of the Project Officers to evaluate the influence of glass fiber filters with high phosphate blanks.*

Based on consultations with the Project Officers, phosphate, $SiO_3^=$, $Cl^-$, colloidal clay and p-benzoquinone were chosen for single interferent investigation and for the pairs and quartet studies, chloride was eliminated from this set. Sulfate concentrations were selected throughout the working range of each method. Table 25 lists the concentrations chosen for single interferent work, while Tables 26, 27, and 28 provide corresponding values for interferent pairs and quartets.

## B. Effect of Single Interferents with Known Sulfate Concentrations

Following the protocol given in Table 25, studies were completed with each of the three sulfate methods, with three determinations for each level. Tables 29, 30, and 31 summarize the interferent results for the MTB, modified Brosset and BC methods, respectively.

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*The glass fiber filters (Gelman No. 65144) recently distributed to the California Air Resources Board from the EPA were determined at AIHL to have 2222 ± 77 µg/8 x 10" sheet of phosphate.

It may be noted in these three tables that the observed sulfate levels with added interferents differ significantly from the nominal sulfate values. These differences for the MTB and Brosset data parallel findings for the accuracy of these techniques using the EPA audit strips. The MTB results, on average, were 3% low compared to 7% low for the audit strips. With the Brosset method, both the zero interferent level samples and the audit strip results averaged about 4% high. With the BC method the relatively poor precision obtained probably accounts for some of the discrepancy between nominal and observed sulfate values. The results with the audit strips indicate values averaging only 1% low. Thus inaccuracy may not be a significant contributor. With the MTB and Brosset data interpretation of interference effects should not be hampered if results are compared to those for the zero interferent levels. With the BC data this same comparison is the most reasonable procedure but the poor precision greatly reduces the reliability of conclusions regarding interference effect.

# TABLE 25

## CALCULATED CONCENTRATIONS FOR SINGLE INTERFERENT STUDIES

| Method | $(SO_4^=)$ µg/ml | $(PO_4^{\equiv})^a$ µg/ml | $(SiO_3^=)^b$ µg/ml | Colloidal clay µg/ml | $(Cl^-)^b$ µg/ml | p-benzoquinone µg/ml |
|---|---|---|---|---|---|---|
| MTB | 10 | 10, 5, 2.5 | 120, 60, 30 | 80, 40, 20 | 40, 20, 10 | 12, 6, 3 |
| | 30 | same | same | same | same | same |
| | 50 | same | same | same | same | same |
| Brosset | 5 | 0.3, 0.15, 0.08 | 30, 15, 8 | 20, 10, 5 | 10,5, 2.5 | 3, 1.5, 0.75 |
| | 8 | same | same | same | same | same |
| | 11 | same | same | same | same | same |
| Barium Chloranilate | 15 | 1.2, 0.6, 0.3 | 120, 60, 30 | 80, 40, 20 | 40, 20, 10 | 12, 6, 3 |
| | 25 | same | same | same | same | same |
| | 40 | same | same | same | same | same |

[a] Maximum atmospheric concentrations: 0.2 µg/m³ $PO_4^{\equiv}$, 0.04 µg/m³ $SO_3^=$ and 0.15 µg/m³ Br. Assuming collection of 2000 m³ on an 8" x 10" filter and extract 3/4" x 8" strip into 50 ml $H_2O$, concentrations: 0.6 µg/ml $PO_4^{\equiv}$, 0.12 µg/ml $SO_3^=$ and 0.46 µg/ml Br. For MTB method the concentrations were increased above those calculated from maximum observed concentrations at the request of the Project Officers.

[b] Extraction of 110 cm² of glass fiber filter in 100 ml $H_2O$ gave 85 µg/ml $SiO_3^=$ (as $SiO_2$) and ≤ 32 µg/ml total halogen (ca 98% $Cl^-$). Data indicate filter the principal source of these ions. For a 3/4" x 8" strip of glass fiber extracted in 50 ml $H_2O$, concentrations: 60 µg/ml $SiO_3^=$ (as $SiO_2$) and 22 µg/ml $Cl^-$.

## Table 26

## CALCULATED CONCENTRATIONS FOR STUDIES OF INTERFERENT PAIRS ($\mu g/ml$)*

| Interferent | Blank | Concentrations of Interferent for Experiment No.<br>I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|---|
| $SiO_3^{=}$ | 0 | 60 | 60 | 60 | 0 | 0 | 0 |
| Clay | 0 | 40 | 0 | 0 | 40 | 40 | 0 |
| $PO_4^{\equiv}$ | 0 | 0 | 10 | 0 | 10 | 0 | 10 |
| p-benzoquinone | 0 | 0 | 0 | 6 | 0 | 6 | 6 |

---

*Concentrations for use with MTB and BC Methods. With Brosset method divide all concentrations by 4.

## TABLE 27

## CALCULATED CONCENTRATIONS FOR STUDIES OF INTERFERENT QUARTETS (μg/ml)*

| Interferent | Blank | Concentrations of Interferent for Experiment No. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | I | II | III | IV | V | VI | VII | VIII | IX |
| $SiO_3^=$ | 0 | 60 | 30 | 60 | 60 | 60 | 90 | 60 | 60 | 60 |
| Clay | 0 | 40 | 40 | 20 | 40 | 40 | 40 | 60 | 40 | 40 |
| $PO_4^{\equiv}$ | 0 | 5 | 5 | 5 | 2.5 | 5 | 5 | 5 | 7.5 | 5 |
| p-benzoquinone | 0 | 6 | 6 | 6 | 6 | 3 | 6 | 6 | 6 | 9 |

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*Concentrations for MTB and BC methods. For the Brosset method divide all concentrations by 4.

## TABLE 28

## SULFATE CONCENTRATIONS FOR STUDY OF INTERFERENT PAIRS AND QUARTETS (μg/ml)

| Method | Working Range | $SO_4^=$ Level 1[a)] | $SO_4^=$ Level 2[b)] |
|---|---|---|---|
| MTB | 7-75 | 25 | 40 |
| Modified Brosset | 3-13 | 5 | 10 |
| Barium chloranilate | 10-50 | 25 | 40 |

a) Approximately one third of the working range

b) Approxiamtely two thirds of the working range

## TABLE 29

## INTERFERENCE EFFECT WITH THE METHYLTHYMOL BLUE METHOD (μg/ml OBSERVED SULFATE)[a]

| Nominal Sulfate Level, μg/ml | 15 | | | | 25 | | | | 40 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Interferent Level, μg/ml[b] | 0 | A | B | C | 0 | A | B | C | 0 | A | B | C |
| Interferent | | | | | | | | | | | | |
| Silicate | 14.0<br>.4 | 14.8<br>.1 | 15.0<br>.03 | 15.6<br>.05 | 24.1<br>.3 | 25.4<br>.3 | 25.6<br>.2 | 26.1<br>.1 | 40.0<br>.05 | 41.5<br>.2 | 42.2<br>.04 | 42.5<br>.05 |
| Chloride | 14.2<br>.3 | 14.4<br>.4 | 14.3<br>.4 | 14.3<br>.4 | 24.1<br>.3 | 24.4<br>.7 | 24.6<br>.7 | 24.6<br>.5 | 39.3<br>.7 | 39.4<br>.8 | 39.6<br>.6 | 39.9<br>.8 |
| Clay | 14.3<br>.2 | 14.7<br>.1 | 15.3<br>.2 | 16.9<br>.3 | 24.6<br>.3 | 25.1<br>.1 | 25.7<br>.2 | 26.9<br>.03 | 39.9<br>.1 | 40.6<br>.2 | 41.4<br>.1 | 42.7<br>.1 |
| p-benzoquinone | 14.3<br>.1 | 14.5<br>.2 | 14.7<br>.1 | 14.9<br>.5 | 24.7<br>.4 | 24.8<br>.2 | 25.3<br>.2 | 25.6<br>.2 | 40.4<br>.2 | 40.5<br>.2 | 41.0<br>.2 | 41.9<br>.1 |
| Nominal Sulfate Level, μg/ml | 10 | | | | 30 | | | | 50 | | | |
| Interferent Level, μg/ml[b] | 0 | A | B | C | 0 | A | B | C | 0 | A | B | C |
| Phosphate | 9.3<br>.2 | 9.7<br>.3 | 10.0<br>.3 | 10.2<br>.3 | 29.1<br>.1 | 30.6<br>.1 | 31.0<br>.2 | 31.6<br>.3 | 49.5<br>.1 | 52.5<br>.1 | 53.0<br>.2 | 53.7<br>.2 |

a. Mean of 3 determinations ± 1σ value shown below mean.

b. Interferent concentration, μg/ml:

| | A | B | C |
|---|---|---|---|
| $PO_4$ | 2.5 | 5 | 10 |
| $SiO_2$ | 30 | 60 | 120 |
| Cl | 10 | 20 | 40 |
| Clay | 20 | 40 | 80 |
| p-bzq | 3 | 6 | 12 |

Table 30

INTERFERENCE EFFECT WITH MODIFIED BROSSET METHOD (μg/ml OBSERVED SULFATE)[a]

| Nominal Sulfate Level, μg/ml | 5 | | | | 8 | | | | 11 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Interferent Level, μg/ml[b] | O | A | B | C | O | A | B | C | O | A | B | C |
| **INTERFERENT** | | | | | | | | | | | | |
| Phosphate | 5.5<br>.1 | 5.3<br>.2 | 5.3<br>.1 | 5.3<br>.2 | 8.0<br>.1 | 7.6<br>.2 | 7.7<br>.4 | 7.8<br>.1 | 11.2<br>.2 | 11.2<br>.04 | 11.2<br>.2 | 11.2<br>.1 |
| Silicate | 5.5<br>.2 | 5.3<br>.2 | 5.0<br>.1 | 5.1<br>.1 | 7.6<br>.04 | 7.7<br>.1 | 7.6<br>.2 | 7.5<br>.2 | 11.6<br>.2 | 11.6<br>.1 | 11.7<br>.1 | 11.6<br>.2 |
| Chloride | 5.5<br>.1 | 5.5<br>.1 | 5.4<br>.1 | 5.3<br>.2 | 7.9<br>.03 | 7.9<br>.2 | 7.9<br>.03 | 7.9[c]<br>.1 | 11.2<br>.1 | 11.2<br>.1 | 11.0<br>.2 | 11.0<br>.2 |
| Clay | 5.0<br>.3 | 5.4<br>.2 | 5.7<br>.2 | 6.0<br>.2 | 8.1<br>.1 | 8.3<br>.1 | 8.6<br>.1 | 8.8<br>.1 | 11.0<br>.2 | 11.6<br>.2 | 12.1<br>.2 | 12.3<br>.2 |
| p-benzoquinone | 5.2<br>.1 | 4.8<br>.1 | 4.7<br>.1 | 4.6<br>.1 | 7.8<br>.1 | 7.8<br>.1 | 7.7<br>.1 | 7.6<br>.1 | 11.8<br>.4 | 11.5<br>.3 | 11.5<br>.4 | 11.3<br>.4 |

a. Mean of three determinations with ± 1σ value shown below mean.

b. Interferent concentrations, μg/ml:

| | A | B | C |
|---|---|---|---|
| $PO_4$ | .08 | .15 | .30 |
| $SiO_2$ | 8 | 15 | 30 |
| Cl | 2.5 | 5 | 10 |
| Clay | 5 | 10 | 20 |
| p-bzq | .75 | 1.5 | 3 |

c. The sulfate value for the "zero" level sample to be compared with this was 8.1 ± .1.

Table 31

## INTERFERENCE EFFECT WITH THE BARIUM CHLORANILATE METHOD (μg/ml OBSERVED SULFATE)[a]

| Nominal Sulfate Level, μg/ml | 15 | | | | 25 | | | | 40 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Interferent Level, μg/ml | O | A | B | C | O | A | B | C | O | A | B | C |
| INTERFERENT | | | | | | | | | | | | |
| Phosphate | 14.3<br>1.7 | 14.9<br>.1 | 17.5<br>1.3 | 16.5<br>4.2 | 23.9<br>2.0 | 25.4<br>2.6 | 26.5<br>5.3 | 26.2<br>2.1 | 38.0<br>1.1 | 38.0<br>1.0 | 37.8<br>1.4 | 38.3<br>.9 |
| Silicate | 14.4<br>2.9 | 14.8<br>3.1 | 14.7<br>2.7 | 14.6<br>1.7 | 25.0<br>2.3 | 26.6<br>2.9 | 24.8<br>1.3 | 28.0<br>5.0 | 38.6<br>.6 | 37.6<br>2.2 | 38.9<br>.9 | 38.7<br>2.3 |
| Chloride | 14.4<br>.3 | 15.0<br>.8 | 16.5<br>1.7 | 15.6<br>.3 | 24.0<br>1.3 | 24.8<br>.4 | 24.2<br>.4 | 25.1<br>.7 | 40.5<br>.6 | 39.2<br>1.8 | 39.8<br>1.3 | 37.9<br>.4 |
| Clay | 14.9<br>.1 | 15.1<br>.3 | 15.8<br>.7 | 16.4<br>.2 | 25.1<br>.6 | 25.5<br>1.5 | 25.5<br>.3 | 26.4<br>1.0 | 38.8<br>.6 | 40.1<br>.8 | 40.6<br>.7 | 40.5<br>.9 |

| Nominal Sulfate Level, μg/ml | 10 | | | | 30 | | | | 50 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Interferent Level, μg/ml | O | A | B | C | O | A | B | C | O | A | B | C |
| p-benzoquinone | 9.9<br>.3 | 9.5<br>.8 | 11.3<br>1.3 | 11.7<br>.8 | 29.6<br>.8 | 29.1<br>.3 | 29.7<br>.7 | 30.8<br>.8 | 49.1<br>.9 | 49.9<br>.6 | 50.4<br>1.0 | 49.1<br>2.3 |

a. Mean of 3 determinations ± 1 σ value shown below mean.

b. Interferent concentration, μg/ml:

| | A | B | C |
|---|---|---|---|
| $PO_4$ | .3 | .6 | 1.2 |
| $SiO_3$ | 30 | 60 | 120 |
| Cl | 10 | 20 | 40 |
| Clay | 20 | 40 | 80 |
| p-bzq | 3 | 6 | 12 |

For the MTB data, the study with phosphate was inadvertently run at 10, 30 and 50 μg/ml sulfate. Aside from the awkwardness of data presentation, this error seemed insufficient to warrant repetition at the correct level. Observed interferences with this method were either negligible or positive in direction. Chloride did not show interference beyond experimental error while silicate and phosphate gave the most interference (up to 11%). While the maximum interference from p-benzoquinone was only +4%, it was observed at all sulfate levels.

With the modified Brosset method, the results with single interferents suggest negligible (i.e. < 5%) effects for phosphate and chloride. Silicate exhibits up to a 10% negative interference at 5 μg/ml sulfate, clay a 10-20% positive interference at 5 and 8 μg/ml sulfate and p-benzoquinone, up to a 12% negative interference at the 5 μg/ml sulfate. In the latter case, small but consistent negative interferences are seen at 8 and 11 μg/ml sulfate as well.

For the BC study, p-benzoquinone was inadvertently run at 10, 30 and 50 μg/ml sulfate instead of 15, 25 and 40. Again, aside from the awkwardness of data presentation, this error seemed insufficient to warrant repetition at the correct sulfate levels.

Interpretation of interference effects with the BC method is made difficult by the relatively poor precision of the method. Coefficients of variation up to 25% at the lowest sulfate levels were seen for triplicate determinations. Nevertheless, all of the interferents except silicate caused measurable ($\geq$ 5% positive) interference at the lowest sulfate level. At higher sulfate, interferences are either < 5% or uncertain because of large standard deviations in the results. The largest interference is shown for p-benzoquinone with 10 $\mu$g/ml sulfate. The bentonite clay suspension generally yielded a negligible effect with possibly a small positive error at the highest clay level. Phosphate exhibited a 10-15% positive interference at 15 and 25 $\mu$g/ml sulfate. Such interference was expected, based on the approximately neutral pH of the method and the resulting formation of insoluble barium phosphate.

## C. Effect of Interferent Pairs with Known Sulfate Concentration

These studies as well as those with interferent quartets were done seeking evidence of interactions between interferents. Tables 32, 33, and 34 summarize results for studies of interferent pairs for the three sulfate methods. As was the case for single interferents the MTB results without added interferents averaged 3% low probably reflecting the same trend as found for EPA audit strips. However, the Brosset results in Table 33 (averaging 4% low) differ in this respect from those with audit strips (4% high) without apparent cause. The BC results for zero interferents were within 2% of the nominal values. Again comparison of results against the blank values is the most reliable strategy for interpretation of results.

With the MTB data, greater percentage interference was observed at the lower sulfate concentration but results at the higher level were qualitatively similar. A comparison of paired results to those

## TABLE 32

## INTERFERENCE EFFECT WITH THE MTB METHOD USING INTERFERENT PAIRS

| Experiment | Interferent | | Interferent Concentration (µg/ml) | | Observed Sulfate at Nominal Sulfate Level (µg/ml)[a] | |
|---|---|---|---|---|---|---|
| | A | B | A | B | 25 | 40 |
| Blank | --- | --- | 0 | 0 | 23.7 ± .03 | 39.8 ± .4 |
| I | $SiO_3^=$ | Clay | 60 | 40 | 26.5 ± .5 | 41.7 ± .6 |
| II | $SiO_3^=$ | $PO_4^\equiv$ | 60 | 10 | 26.7 ± .4 | 43.7 ± .3 |
| III | $SiO_3^=$ | p-bzq[b] | 60 | 6 | 25.1 ± .4 | 41.9 ± .3 |
| IV | Clay | $PO_4^\equiv$ | 40 | 10 | 26.6 ± .3 | 43.0 ± .07 |
| V | Clay | p-bzq | 40 | 6 | 26.2 ± .2 | 41.6 ± .4 |
| VI | $PO_4^\equiv$ | p-bzq | 10 | 6 | 27.7 ± .2 | 43.6 ± .6 |

---

a. Mean ± 1 $\sigma$ for three determinations.

b. p-benzoquinone, a model yellow chromophore.

c. A fresh clay suspension was prepared from kaolinite clay in place of the bentonite clay which was used up in the single interferent work. The light scattering of a 60 µg/ml kaolinite suspension was equivalent to that from 100 µg/ml bentonite.

Table 33

INTERFERENCE EFFECT WITH MODIFIED BROSSET METHOD USING INTERFERENT PAIRS

| Experiment | Interferent | | Interferent Concentration (μg/ml) | | Observed Sulfate at Nominal Sulfate Level (μg/ml)[a] | |
|---|---|---|---|---|---|---|
| | A | B | A | B | 5 | 10 |
| Blank | --- | --- | 0 | 0 | 4.9 ± .1 | 9.4 ± .2 |
| I | $SiO_3^=$ | Clay[c] | 15 | 10 | 4.9 ± .3 | 9.7 ± .2 |
| II | $SiO_3^=$ | $PO_4^{\equiv}$ | 15 | 2.5 | 5.1 ± .2 | 10.4 ± .1 |
| III | $SiO_3^=$ | p-bzq[b] | 15 | 1.5 | 5.0 ± .2 | 9.8 ± .3 |
| IV | Clay | $PO_4^{\equiv}$ | 10 | 2.5 | 5.0 ± .1 | 10.2 ± .2 |
| V | Clay | p-bzq | 10 | 1.5 | 4.9 ± .2 | 9.8 ± .2 |
| VI | $PO_4^{\equiv}$ | p-bzq | 2.5 | 1.5 | 4.9 ± .1 | 9.9 ± .4 |

---

a. Mean ± 1 σ for three determinations.

b. p-benzoquinone, a model yellow chromophore.

c. A fresh clay suspension was prepared from kaolinite clay in place of the bentonite clay which was used up in the single interferent work. The light scattering of a 60 μg/ml kaolinite suspension was equivalent to that from 100 μg/ml bentonite.

## TABLE 34

## INTERFERENCE EFFECT WITH BARIUM CHLORANILATE METHOD USING INTERFERENT PAIRS

| Experiment | Interferent | | Interferent Concentration (μg/ml) | | Observed Sulfate at Nominal Sulfate Level (μg/ml)[a] | |
|---|---|---|---|---|---|---|
| | A | B | A | B | 25 | 40 |
| Blank | --- | --- | 0 | 0 | 24.9 ± .5 | 39.3 ± .2 |
| I | $SiO_3^{=}$ | Clay | 60 | 40 | 24.7 ± .7 | 39.3 ± .8 |
| II | $SiO_3^{=}$ | $PO_4^{\equiv}$ | 60 | 10 | 26.1 ± .9 | 41.9 ±1.0 |
| III | $SiO_3^{=}$ | p-bzq[b] | 60 | 6 | 25.3 ± .3 | 40.1 ± .8 |
| IV | Clay | $PO_4^{\equiv}$ | 40 | 10 | 26.8 ±1.2 | 41.4 ±1.1 |
| V | Clay | p-bzq | 40 | 6 | 25.7 ± .2 | 39.6 ± .2 |
| VI | $PO_4^{\equiv}$ | p-bzq | 10 | 6 | 27.8 ± .4 | 41.7 ±1.1 |

---

[a] Mean ± 1 $\sigma$ for three determinations.

[b] p-benzoquinone, a model yellow chromophore.

[c] A fresh clay suspension was prepared from kaolinite clay in place of the bentonite clay which was used up in the single interferent work. The light scattering of a 60 μg/ml kaolinite suspension was equivalent to that from 100 μg/ml bentonite.

obtained individually is given in Table 35 for the lower sulfate level. The paired results are seen to often exceed 10% interference and are roughly additive from the results for the individual interferents (i.e. no interaction is evident).

With the modified Brosset method, greater interferences were observed at the higher sulfate level. Table 36 compares results for interferents singly and in pairs at 10.5 ± .5 μg/ml sulfate. The results for clay-phosphate, clay-p-benzoquinone and silicate-clay appear to be somewhat less than additive. With silicate-phosphate, the pair result exceeds significantly the sum of the interference effects individually. However, as may be seen comparing Tables 25 and 26, the phosphate concentration used in the paired interferent studies for the Brosset (and BC) method was about a factor of 10 higher than that used in the single interferent work. Thus, no conclusions are possible regarding non-additivity for paired interferents involving phosphate.

For the BC method, the study with interferent pairs was done at sulfate levels for which only phosphate proved to be a significant interferent in single interferent experiments. The pair results summarized in Table 34 indicate, in all cases, interferences < 12%. In contrast to the corresponding Brosset data, similar interference is observable at both sulfate levels studied. Table 37 compares these results to those for the interferents individually. The paired interferent results are roughly predictable from those for the single interferents (i.e. no interaction is evident). The scatter in the data make conclusions tenuous, however.

## TABLE 35

## COMPARISON OF RESULTS OF SINGLE AND PAIRED INTERFERENTS WITH THE MTB METHOD[a]

| Interferent Pair | | A + B Result[b] | Individual Results[c] | | $\frac{\text{A + B Result}}{\Sigma\ \text{Indiv. Results}}$ x 100 |
|---|---|---|---|---|---|
| A | B | | A | B | |
| $SiO_3^{=}$ | clay | ++ | + | + | 82[f] |
| $SiO_3^{=}$ | $PO_4^{\equiv}$ | ++ | + | + | 75 |
| $SiO_3^{=}$ | p-bzq[d] | + | + | 0[e] | 67 |
| clay | $PO_4^{\equiv}$ | ++ | + | + | 66[f] |
| clay | p-bzq | ++ | + | 0[e] | 100[f] |
| $PO_4^{\equiv}$ | p-bzq | ++ | + | 0[e] | 129 |
| | | | | | Mean: 87 ± 24 |

---

a. 0 equals ≤ 5% interference
+ equals > 5% positive interference
++ equals > 10% positive interference

b. Results at 25 μg/ml sulfate. At 40 μg/ml sulfate, interferences are less pronounced.

c. Results in the range 25-30 μg/ml sulfate with interferent concentrations as used in paired study.

d. p-benzoquinone

e. A consistent positive interference of up to 4% is seen at all sulfate levels studied.

f. Corrected for use of kaolinite rather than bentonite.

## TABLE 36

## COMPARISON OF RESULTS OF SINGLE AND PAIRED INTERFERENTS WITH THE BROSSET METHOD

| Interferent Pair | | A + B Result[a] | Individual Results[b] | | $\frac{\text{A + B Result}}{\Sigma \text{ Indiv. Results}}$ x 100 |
|---|---|---|---|---|---|
| A | B | | A | B | |
| $SiO_3^=$ | clay | 0 | 0 | + | 25 |
| $SiO_3^=$ | $PO_4^{\equiv}$ | ++ | 0 | 0 | — |
| $SiO_3^=$ | p-bzq[c] | 0 | 0 | 0 | — |
| clay | $PO_4^{\equiv}$ | + | + | 0[d] | 67[d] |
| clay | p-bzq | 0 | + | 0 | 44 |
| $PO_4^{\equiv}$ | p-bzq | 0 | 0 | 0 | — |

---

a. Results at 10 μg/ml sulfate

0 equals ≤ 5% interference
- equals > 5% negative interference
+ equals > 5% positive interference
++ equals > 10% positive interference

b. Results at 11 μg/ml sulfate

c. p-benzoquinone

d. Results of questionable value since phosphate concentration 10 times lower than used in paired experiment.

## TABLE 37

## COMPARISON OF RESULTS OF SINGLE AND PAIRED INTERFERENTS WITH THE BARIUM CHLORANILATE METHOD

| Interferent Pair | | A + B Result[a] | Individual Results[b] | | $\frac{\text{A + B Result}}{\Sigma \text{ Indiv. Results}} \times 100$ |
|---|---|---|---|---|---|
| A | B | | A | B | |
| $SiO_3^=$ | clay | 0 | 0 | 0 | -- |
| $SiO_3^=$ | $PO_4^{\equiv}$ | + | 0 | +[d] | 50[e] |
| $SiO_3^=$ | p-bzq[c] | 0 | 0 | 0 | -- |
| clay | $PO_4^{\equiv}$ | + | 0 | +[d] | 56[e,f] |
| clay | p-bzq | 0 | 0 | 0 | 80[f] |
| $PO_4^{\equiv}$ | p-bzq | + | +[d] | 0 | 121[e] |
| | | | | Mean: | 77 ± 32 |

---

[a] a. Results at 25 and 40 μg/ml sulfate. See Table 35 for definition of symbols.

[b] b. Results in the range 25-50 μg/ml sulfate with interferent concentrations as used in paired study except for $PO_4^{\equiv}$.

[c] c. p-benzoquinone

[d] d. At 25 μg/ml only

[e] e. Assumes a ceiling on phosphate interference of 2.4 μg/ml apparent sulfate at > 1.2 μg/ml phosphate.

[f] f. Corrected for use of kaolinite rather than bentonite clay

## D. Effect of Interferent Quartets with Known Sulfate Concentrations

The intent of this study was first, to evaluate the combined effect of four interferents on sulfate determination and secondly, to evaluate the influence of individual interferents in the presence of a more realistic matrix. The procedure was to systematically vary the concentration of one interferent at a time to concentrations equal to 1/2 and 3/2 times the level chosen as relevant for study. Tables 38, 39 and 40 report results of this study done at two sulfate concentrations with the three sulfate methods. Just as with the single and paired interferent studies the zero interferent level sulfate values for the quartet studies often differed from the nominal values. With the MTB method, results averaged 4% low; with the Brosset technique, results averaged 2% high and with the BC procedure 4% low. These MTB and Brosset results parallel the trends observed with the EPA sulfate audit strips. The BC results here indicate substantially greater error than was obtained with the audit strips but the poor precision of the analyses hamper conclusions (e.g. all results at 25 μg/ml are within 2 σ of the zero solution). Calculation of interference effects by comparisons with blank solution results should provide reasonably accurate and precise results, at least for the MTB and Brosset techniques.

For the MTB method, similar relative interference effects were observed at both 25 and 40 μg/ml. As with the pairs, combined interferences often exceeded 10%. A comparison of quartet and individual interferent results, shown in Table 41, reveals that the quartet

## TABLE 38

## INTERFERENCE EFFECT WITH MTB METHOD USING INTERFERENT QUARTETS

| Experiment | Interferent Concentration (µg/ml) | | | | Observed Sulfate at Nominal Sulfate Level (µg/ml)[b] | |
|---|---|---|---|---|---|---|
| | $SiO_3^=$ | Clay[c] | $PO_4^{\equiv}$ | p-bzq[a] | 25 | 40 |
| Blank | 0 | 0 | 0 | 0 | 23.5 ± .3 | 38.9 ± .2 |
| I | 60 | 40 | 5 | 6 | 26.4 ± .2 | 43.1 ± .2 |
| II | 30 | 40 | 5 | 6 | 26.4 ± .2 | 43.2 ± .2 |
| III | 60 | 20 | 5 | 6 | 26.1 ± .1 | 43.1 ± .2 |
| IV | 60 | 40 | 2.5 | 6 | 26.4 ± .2 | 43.0 ± .2 |
| V | 60 | 40 | 5 | 3 | 25.9 ± .1 | 41.8 ± .2 |
| VI | 90 | 40 | 5 | 6 | 26.7 ± .3 | 43.8 ± .3 |
| VII | 60 | 60 | 5 | 6 | 27.4 ± .1 | 44.0 ± .4 |
| VIII | 60 | 40 | 7.5 | 6 | 26.9 ± .4 | 44.0 ± .2 |
| IX | 60 | 40 | 5 | 9 | 26.6 ± .3 | 44.0 ± .2 |

---

a. p-benzoquinone

b. Mean ± 1 σ for 3 trials

c. See footnote c, Table 32

## TABLE 39

## INTERFERENCE EFFECT WITH MODIFIED BROSSET METHOD USING INTERFERENT QUARTETS

| Experiment | Interferent Concentration (µg/ml) | | | | Observed Sulfate at Nominal Sulfate Level (µg/ml)[b] | |
|---|---|---|---|---|---|---|
| | $SiO_3^=$ | Clay[c] | $PO_4^{\equiv}$ | p-bzq[a] | 5 | 10 |
| Blank | 0 | 0 | 0 | 0 | 5.2 ± .2 | 10.0 ± .2 |
| I | 15 | 10 | 1.25 | 1.5 | 5.0 ± .1 | 10.2 ± .2 |
| II | 7.5 | 10 | 1.25 | 1.5 | 5.2 ± .3 | 10.6 ± .2 |
| III | 15 | 5 | 1.25 | 1.5 | 5.4 ± .1 | 10.7 ± .3 |
| IV | 15 | 10 | .63 | 1.5 | 5.0 ± .1 | 10.6 ± .3 |
| V | 15 | 10 | 1.25 | .75 | 5.1 ± .3 | 10.7 ± .5 |
| VI | 22.5 | 10 | 1.25 | 1.5 | 5.1 ± .2 | 10.9 ± .2 |
| VII | 15 | 15 | 1.25 | 1.5 | 5.2 ± .1 | 10.9 ± .1 |
| VIII | 15 | 10 | 1.88 | 1.5 | 5.2 ± .02 | 10.8 ± .1 |
| IX | 15 | 10 | 1.25 | 2.25 | 5.1 ± .4 | 10.1 ± .2 |

[a] b-benzoquinone

[b] mean ± 1 σ for 3 trials

[c] see footnote c, Table 33

## TABLE 40

## INTERFERENCE EFFECT WITH BARIUM CHLORANILATE METHOD USING INTERFERENT QUARTETS

| Experiment | Interferent Concentration (µg/ml) | | | | Observed Sulfate at Nominal Sulfate Level (µg/ml)[b] | |
|---|---|---|---|---|---|---|
| | $SiO_3^{=}$ | Clay | $PO_4^{\equiv}$ | p-bzq[a] | 25 | 40 |
| Blank | 0 | 0 | 0 | 0 | 23.9 ± 1.4 | 38.7 ± .9 |
| I | 60 | 40 | 5 | 6 | 25.8 ± 1.2 | 40.1 ± .7 |
| II | 30 | 40 | 5 | 6 | 25.6 ± 1.6 | 40.4 ± .7 |
| III | 60 | 20 | 5 | 6 | 26.0 ± .9 | 41.8 ± .2 |
| IV | 60 | 40 | 2.5 | 6 | 25.5 ± .7 | 41.0 ± 1.0 |
| V | 60 | 40 | 5 | 3 | 24.0 ± .3 | 40.0 ± .9 |
| VI | 90 | 40 | 5 | 6 | 25.7 ± .3 | 41.4 ± 1.0 |
| VII | 60 | 60 | 5 | 6 | 25.5 ± 1.4 | 41.3 ± .9 |
| VIII | 60 | 40 | 7.5 | 6 | 25.7 ± .5 | 42.0 ± 1.4 |
| IX | 60 | 40 | 5 | 9 | 25.6 ± .9 | 42.5 ± .9 |

---

[a] p-benzoquinone

[b] Mean ± 1 σ for 3 trials

## TABLE 41

## COMPARISON OF RESULTS OF SINGLE AND INTERFERENT QUARTETS WITH THE MTB METHOD

| Experiment | Individual Result[b]<br>$SiO_3^=$ | <br>Clay | <br>$PO_4^\equiv$ | <br>p-bzq[c] | $\frac{\text{Combined}}{\Sigma \text{ Individual}} \times 100$ |
|---|---|---|---|---|---|
| I | + | 0 | + | 0 | 49 |
| II | $\underline{\underline{+}}$ | 0 | + | 0 | 51 |
| III | + | $\underline{\underline{0}}$ | + | 0 | 73 |
| IV | + | 0 | $\underline{\underline{+}}$ | 0 | 53 |
| V | + | 0 | + | $\underline{\underline{0}}$ | 44 |
| VI | $\underline{+}$ | 0 | + | 0 | 52 |
| VII | + | $\underline{0}$ | + | 0 | 57 |
| VIII | + | 0 | $\underline{+}$ | 0 | 55 |
| IX | + | 0 | + | $\underline{0}$ | 50 |
| | | | | Mean | 54 ± 8 |

---

a. At 25 and 40 µg/ml sulfate, See Table 35 for definition of symbols.

b. In the range 25-50 µg/ml sulfate. A double underscore denotes an interferent concentration cut in half. A single underscore denotes an interferent concentration increased by 50%.

c. See footnote e, Table 35.

results are about half the sum of the individual results. Systematically increasing the concentration of single interferents reveals either a negligible change or an increase in observed sulfate.

For the Brosset results with interferent quartets the following observations can be made:

1. In no case does the observed interference exceed 10% of the nominal sulfate concentration.
2. As in the study with interferent pairs, interference is more pronounced at the higher sulfate level, and all interferences are positive.
3. Except for p-benzoquinone, the results of varying one interferent at a time show no consistent trend. At 10 μg/ml, both increasing and decreasing interferent concentrations gives higher values than the initial experiment (I). With p-bzq, results are consistent with a negative interference.

The combined results are compared to those of the individual interferents in Table 42. The combined results range from 11 to 150% of the effect predicted. Relatively small interference effects and a somewhat poorer precision of the method compared to the MTB probably account for the scattered results.

For the BC method, Table 40 reports results of this study from which we make the following observations:

1. In no case does the observed interference exceed 10% of the nominal sulfate level.

## TABLE 42

## COMPARISON OF RESULTS OF SINGLE INTERFERENT QUARTETS WITH THE BROSSET METHOD AT 10-11 μg/ml SULFATE[a]

| | Individual Result[b] | | | | |
|---|---|---|---|---|---|
| **Experiment** | $SiO_3^=$ | Clay | $PO_4^=$ | p-bzq | $\frac{\text{Combined}}{\Sigma\ \text{Individual}} \times 100$ |
| I | 0 | + | 0 | 0 | 22 |
| II | $\underline{\underline{0}}$ | + | 0 | 0 | 67 |
| III | 0 | $\underline{\underline{+}}$ | 0 | 0 | 86 |
| IV | 0 | + | $\underline{\underline{0}}$ | 0 | 150 |
| V | 0 | + | 0 | $\underline{\underline{0}}$ | 130 |
| VI | $\underline{0}$ | + | 0 | 0 | 100 |
| VII | 0 | $\underline{+}$ | 0 | 0 | 122 |
| VIII | 0 | + | $\underline{0}$ | 0 | 113 |
| IX | 0 | + | 0 | $\underline{0}$ | 11 |
| | | | | Mean | 89 ± 48 |

---

a. See Table 35 for definitions of symbols.

b. At 11 μg/ml sulfate. A double underscore denotes an interferent concentration cut in half. A single underscore denotes an interferent concentration increased by 50%.

2. As in the study of interferent pairs, interference effects are similar at both sulfate levels studied.
3. Varying systematically the concentrations of single interferents reveals no consistent pattern. Possibly the most significant result is the increase in apparent sulfate on increasing the p-benzoquinone level from 6 to 9 μg/ml at 40 μg/ml sulfate. The increase, about 6%, is similar to the 4% interference observed in single interferent studies.

The quartet results are compared to those found in studies of interferent individually in Table 43. As with the MTB method, the quartet results are generally about half of those predicted from the individual interferents.

## E. Summary and Discussion of Interference Studies

Table 44 summarizes results of the single interferent studies for the three sulfate methods and generally reflects the sensitivity of each method around its mid-range. The modified Brosset method is subject to the fewest interferents and the MTB, the greatest number from the interferents selected.

Interference effects for the MTB and a manual modified Brosset method have been previously reported.[1] For the MTB method, a positive interference from phosphate was observed only at the upper end of the working range. The present results indicate substantial sensitivity to phosphate at lower sulfate levels as well. Previously, colloidal clay

## TABLE 43

## COMPARISON OF RESULTS OF SINGLE AND INTERFERENT QUARTETS WITH THE BARIUM CHLORANILATE METHOD AT 25 AND 40 μg/ml SULFATE[a]

|  | Individual Result[b] |  |  |  |  |
|---|---|---|---|---|---|
| Experiment | SiO$_3^=$ | Clay | PO$_4^{\equiv}$ | p-bzq | $\frac{\text{Combined}^c}{\Sigma\ \text{Individual}} \times 100$ |
| I | 0 | 0 | + | 0 | 56 |
| II | $\underline{\underline{0}}$ | 0 | + | 0 | 50 |
| III | 0 | $\underline{\underline{0}}$ | + | 0 | 75 |
| IV | 0 | 0 | $\underline{\underline{+}}$ | 0 | 47 |
| V | 0 | 0 | + | $\underline{\underline{0}}$ | 3 |
| VI | $\underline{0}$ | 0 | + | 0 | 53 |
| VII | 0 | $\underline{0}$ | + | 0 | 38 |
| VIII | 0 | 0 | $\underline{+}$ | 0 | 53 |
| IX | 0 | 0 | + | $\underline{0}$ | 41 |
|  |  |  |  |  | Mean 46 ± 19 |

---

a. See Tables 35 and 42 for definition of symbols.

b. In the range 25-50 μg/ml sulfate.

c. Assumes a ceiling of 2.4 μg/ml apparent sulfate for phosphate interference above 1.2 μg/ml phosphate.

## TABLE 44

## SUMMARY OF SINGLE INTERFERENT RESULTS[a)][b)]

| Interferent | MTB | Brosset | BC |
|---|---|---|---|
| silicate | + | 0 | 0 |
| phosphate | + | 0 | + |
| colloidal clay | + | + | 0 |
| p-benzoquinone | 0[c] | 0[e] | 0 |
| chloride | 0 | 0 | +[d] |

[a] 0 equals ≤ 5% interference
+ equals > 5% positive interference
++ equals > 10% positive interference

[b] Sulfate level at mid to upper range of each method except as noted

[c] A consistent + 4% interference observed at all sulfate levels

[d] Observed only at ≤ mid-range of this method

[e] Up to a 4% negative interference is observed at the mid and upper range and up to a 12% negative interference near the bottom of the sulfate range.

exhibited substantial positive interference at mid-range sulfate levels which is consistent with present results. The small positive interference by a yellow chromophore is consistent with the absence of any blank correction with this method. The positive interference by silicate was not previously observed in this study. While the cause of the differences in observations is unknown, the present results, reflecting three independent trials rather than a single trial as used earlier, are considered more reliable.

The previous studies with a modified Brosset method using dioxane and acetone as solvents did not show interference by colloidal clay, in contrast to the current results using isopropanol. A small negative interference by p-benzoquinone was also observed in the earlier work.

Interference effects for the BC method were previously reported by workers at TRW who observed substantial interference by chloride at 100 μg/ml levels of interferent.[5] The present results indicate a greater sensitivity to chloride.

Studies of interferent quartets indicate about half the expected effect with the MTB and BC methods implying some degree of interaction. However, studies of interferent pairs has generally failed to reveal clear evidence of such interactions; the results with interferent pairs are, with one exception, roughly predictable as the sum of the effects of the interferents individually. The exception is the case of the phosphate-silicate pair with the modified Brosset method. The results for the pair reveal > 10% positive interference while exhibiting negligible effects individually. However, the much higher phosphate concentration used in the paired interferent studies vitiates comparisons of single and paired interferents results.

## F. Correction of Atmospheric Sample Results for Interference Effects

Having analyzed at least selected samples for a number of interferents, these data may be used to estimate the maximum likely effects of these interferents on the analysis of a given filter type by a given method. Table 45 compiles calculated maximum interferent concentrations for each filter type and analytical method. The concentrations differ by analytical method since differing degrees of dilution were used to achieve sulfate concentrations in the working range of each method. Approximate average dilution factors were used for the calculation. The assumptions necessary to construct such a table are listed as footnotes.

Using these estimated maximum concentrations and the results for the single interferent studies (Tables 29, 30, 31), the maximum estimated errors are calculated for the mid-range sulfate level of each method in Table 46.

The principal conclusions of these calculations are:

1. Significant errors due to the interferents studied are possible with all filter media.
2. Due primarily to the small air volume sampled, the error, in $\mu g/m^3$, is substantially greater for the 126 mm glass fiber compared to the glass fiber hi-vol filters.

## Table 45

## MAXIMUM CALCULATED INTERFERENT CONCENTRATIONS UNDER CONDITIONS USED FOR MTB, BROSSET AND BC ANALYSES (μg/ml)[a]

| | | Fluoropore | 8 x 10" Glass | 126 mm Glass | 126 mm Quartz |
|---|---|---|---|---|---|
| **Silicate** | MTB | 11 | 66 | 84 | 41 |
| | Brosset | 4 | - | 17 | 14 |
| | BC | 11 | 66 | 49 | 29 |
| **Phosphate** | MTB | .2 | .5 | .5 | .03 |
| | Brosset | .05 | - | .1 | .01 |
| | BC | .2 | .5 | .3 | .02 |
| **Chloride and Bromide** | MTB | ~ 0 | 24 | 31 | 5 |
| | Brosset | ~ 0 | - | 6 | 2 |
| | BC | ~ 0 | 24 | 18 | 4 |
| **Sulfite** | MTB | .04 | .14 | .09 | .09 |
| | Brosset | .01 | - | .02 | .03 |
| | BC | .04 | .14 | .05 | .06 |
| **Colloidal Clay** | MTB | 6[b] | 40 | 38 | 24[b] |
| | Brosset | 2[b] | - | 8 | 8[b] |
| | BC | 6[b] | 40 | 22 | 17[b] |
| **p-benzoquinone**[b] | MTB | 1 | 6 | 5 | 5 |
| | Brosset | .4 | - | 1 | 1 |
| | BC | 1 | 6 | 3 | 3 |

---

a. Based on observed maximum concentrations corrected for average degree of dilution used for each method.

b. Calculated assuming filter blank = 0.

Table 46

## ESTIMATED MAXIMUM ERROR FOR ATMOSPHERIC SAMPLES AT MID-RANGE SULFATE CONCENTRATIONS[a,b]

| | | | | | | | | Combined Error[c] | |
|---|---|---|---|---|---|---|---|---|---|
| **Filter** | | $SiO_3^=$ | $PO_4^{\equiv}$ | $Cl^-$ | $SO_3^=$ | Clay | p-bsq | µg/ml | µg/m³ |
| **Fluoropore** | **MTB** | + .5 | + .1 | 0 | 0 | + .2 | 0 | + .8 | +1.1 |
| | **Brosset** | 0 | - .3 | 0 | 0 | + .1 | 0 | - .2 | - .3 |
| | **BC** | 0 | +1.0 | 0 | 0 | + .1 | 0 | +1.1 | +1.5 |
| **8 x 10" Glass** | **MTB** | +1.5 | + .3 | +.5 | +.1 | +1.1 | + .6 | +4.1 | + .5 |
| | **Brosset** | - | - | - | - | - | - | - | - |
| | **BC** | 0 | +2.2 | 0 | +.1 | + .4 | 0 | +2.7 | + .3 |
| **126 mm Glass** | **MTB** | +1.7 | + .3 | +.5 | +.1 | +1.0 | + .5 | +4.1 | +1.6 |
| | **Brosset** | 0 | - .4 | 0 | 0 | + .4 | 0 | 0 | 0 |
| | **BC** | 0 | +1.5 | 0 | +.1 | + .4 | 0 | +2.0 | + .8 |
| **126 mm Quartz** | **MTB** | +1.4 | 0 | +.1 | +.1 | + .6 | + .5 | +2.7 | +1.0 |
| | **Brosset** | 0 | 0 | 0 | 0 | + .4 | 0 | + .4 | + .2 |
| | **BC** | 0 | 0 | 0 | +.1 | + .4 | 0 | + .5 | + .2 |

a. Estimations based on Tables 29-31 and 45

b. µg/ml sulfate, except as noted.

c. Errors taken as approximately additive.

3. The modified Brosset method results are subject to minimal interference effects due to the greater dilution employed and the lesser sensitivity of this method to interferents.

## VIII. EVALUATION OF ARTIFACT SULFATE FORMATION WITH ATMOSPHERIC SAMPLES

The phenomenon of fixation of $SO_2$ on a filter surface by interaction with the filter medium and particulate matter already collected, and subsequent analysis as water soluble sulfate, is referred to as artifact sulfate formation. Nearly all studies to date have concluded that $SO_2$-filter interactions predominate over $SO_2$-particulate interactions.

The significance of filter choice is illustrated in Table 47, taken from studies by R. Coutant, Battelle Columbus Lab. Sampling was done from a manifold drawing ambient air into two equivalent tubes. On each tube, four filter holders were installed permitting simultaneous sampling. For the work described in Table 47, 150 ppb $SO_2$ was introduced into one of the manifold tubes upstream from the samplers. Thus, the sulfate sampled from the tube with added $SO_2$ should reflect any incremental increase in artifact sulfate formed due to this $SO_2$. For the two high pH glass fiber filters, the increase in observed sulfate was 7 to 8 $\mu g/m^3$. Comparing the glass fiber with the neutral cellulose ester and Teflon filters, the observed sulfate levels were substantially higher. While filter pH may not be the only factor controlling artifact sulfate formation via $SO_2$ sorption, it appears to be dominant.

The filter media used in the two years of sampling for the joint AIHL-EPA study are the following:

| Summer 1974 | Summer 1975 |
|---|---|
| Fluoropore FALP, 37 mm | Fluoropore FALP, 37 mm |
| Gelman glass fiber batch 8188 (similar to Gelman A) 8 x 10" | Gelman AE, 8 x 10" |
| | Gelman AE, 126 mm |
| | Tissue quartz 2500 QAO, 126 mm (Pallflex) |

## TABLE 47

## OBSERVED SULFATE CONCENTRATIONS IN 24-HOUR SAMPLING IN COLUMBUS, OHIO[a]

| | | Sulfate (μg/m$^3$)[b] | |
|---|---|---|---|
| | | Without added $SO_2$ | With added $SO_2$ |
| Filter | Filter pH | (47-99 ppb $SO_2$)[c] | (199-250 ppb $SO_2$) |
| MSA 1106BH (glass) | 9.2 | 29 | 35 |
| Gelman AE (glass) | 9.4 | 31 | 39 |
| Celotate (cellulose acetate) | 6.7 | 19 | 21 |
| Mitex (Teflon) | 7.0 | 18 | 19 |

[a] Source: R. Coutant, paper presented at 172nd American Chemical Society National Meeting, San Francisco, August 1976, and Progress Report to EPA, Contract No. 68-02-1784, September 1975.

[b] Sampling done at ca. 13 cfm with 142 mm filters.

[c] The range in ambient $SO_2$ concentration.

Table 48 summarizes filter pH values for the media used in the current program based on the Battelle Study. Where experimental values are not available, they are estimated based on values for similar filters evaluated at Battelle.

These data suggest that there is relatively little difference between the glass fiber filters used in the first and second year's sampling. In the presence of significant levels of $SO_2$, artifact sulfate formation should follow the order:

Gelman Batch 8188 $\simeq$ Gelman AE > Pallflex Quartz > Fluoropore

Recent studies by Pierson et al[4] confirm that Pallflex Quartz 2500 QAO and Fluoropore filters do provide minimal artifact sulfate, with the Fluoropore filter the more inert.

Based on these studies, efforts at AIHL were directed toward evaluating the extent of artifact sulfate formation on Gelman AE filters. Such an evaluation requires, at least, knowledge of ambient $SO_2$ concentrations. Using monitoring network results (one-hour average values obtained by the conductivity method) 24-hour average $SO_2$ concentrations could be calculated for particulate sampling on days 1-5 at the urban site (106) following the same sampling schedule (1300-1300 hours of the following day) as used for particulate collection.

## Table 48

## THE pH OF THE FILTER MEDIA USED IN THE TWO YEAR EPA-AIHL STUDY[a]

| Filter Type | pH[b] |
|---|---|
| Fluoropore, FALP | EST. 7[c] |
| Pallflex Tissue Quartz, 2500 QAO | EST. 8[d] |
| Gelman Batch 8188[e] | 8.9 |
| Gelman AE | 9.3 |

---

a. Data from R. Coutant, Progress Reports to EPA, Contract No. 68-02-1784.

b. By ASTM D-202.

c. Based on value 7.0 for Mitex (Teflon) filters.

d. Based on value 8.1 for Pallflex tissue quartz QAST.

e. This filter type is designated Gelman AA in the Battelle study.

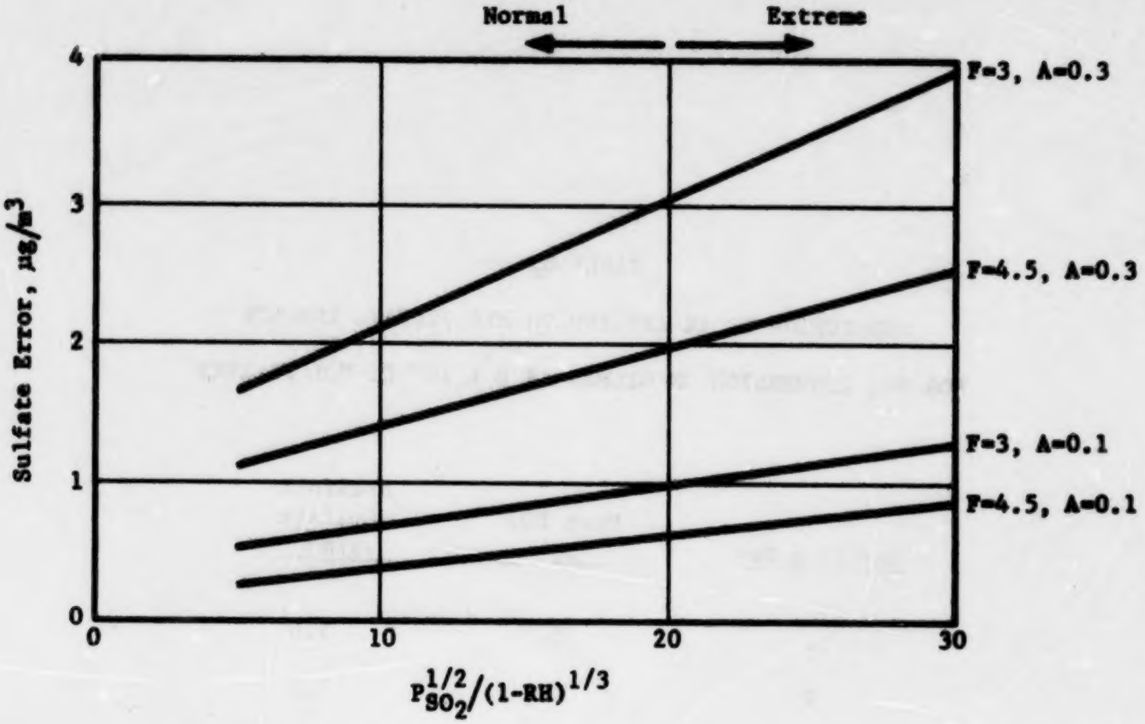
Coutant's studies of artifact sulfate formation are summarized in Figure 22. Using this information, his measured alkalinity for Gelman AE ($4 \times 10^{-2}$ meq/g of filter or .3 $\mu g/cm^2$) and the flow rate for the hi-vol (4.0 $m^3/cm^2$), Table 49 summarized the extent of artifact sulfate formation expected from the $SO_2$ levels given. Since relative humidity data were not available, an average humidity of 60% was assumed. Using Figure 22, an absolute error of 20% in the average R.H. would lead to an error of ca. 0.2 $\mu g/m^3$ in the estimated sulfate error. These data indicate a sulfate error in the range 1.3-1.7 $\mu g/m^3$ for 24-hour, 8 x 10" Gelman AE hi-vol filter samples.

A shortcoming of this calculation is the reliance on $SO_2$ determination by the conductimetric measurement method which is subject to substantial positive interferences. Thus, use of the present $SO_2$ data may lead to some overestimates of the expected artifact sulfate levels. In addition, interpolation is necessary to calculate results for the flow and alkalinity of the present samples and, for $SO_2$ concentrations below 21 ppb, extrapolation of the curve is necessary.

## TABLE 49

## CORRECTION TO BE APPLIED TO MTB SULFATE RESULTS FOR $SO_2$ CONVERSION ON GELMAN AE 8 X 10" HI-VOL FILTERS

| Sampling Day | Mean $SO_2$ ppb | Artifact Sulfate $\mu g/m^3$ |
|---|---|---|
| 1 | 15 | 1.6 |
| 2 | 21 | 1.7 |
| 3 | 4 | 1.3 |
| 4 | 11 | 1.5 |
| 5 | 6 | 1.4 |



**Presented by R.W. Coutant, A.C.S. Meeting, San Francisco, August 1976, "Effects of Environmental Variables on the Collection Efficiency of Atmospheric Sulfate".**

**F = flow, $m^3/cm^2$**

**A = alkalinity, $\mu eq/cm^2$ of filter**

**$P_{SO_2}$ = ppb $SO_2$**

**R.H. = relative humidity expressed as a fraction**

Figure 22. Artifact sulfate in filter sampling.

## IX. COMPARISON OF SULFATE RESULTS ON DIFFERENT FILTER MEDIA

The observed concentration of sulfate extracted from a given filter medium reflects at least five factors:

A. The correct atmospheric sulfate level

B. Artifact sulfate formation

C. Interferents extracted from the filters

D. Interferents extracted from the particulate matter

E. Errors in flow calibration of samplers

Factor E cannot be directly measured with the data available. However, such effects should result in a systematic bias in results for a given filter type regardless of the analytical method used. Sulfate results are compared by filter type in Tables 50, 51 and 52. These compile results by sampling day obtained on the different filter media using the MTB, Brosset and BC methods, respectively. No systematic bias in results is evident suggesting that flow calibration errors are relatively insignificant.

To test the significance of differences in results among the different filter types as implied by the ratios of means, a subset of samples obtained on the same days with all filter media was tested for mean differences and the significance of the difference by the Wilcoxon signed rank test. The results, shown in Tables 53, 54 and 55 are consistent with implications from the ratios of means; with the MTB method only the 126 mm quartz and "fine" Fluoropore are not significantly different at $\geq$ 95% significance level. Similarly, with the Brosset method only the glass and quartz results are not significantly different. Finally, with the BC method, none of the paired results are significantly different at $\geq$ 95% confidence level probably reflecting the poor precision of the method.

With the MTB method, the 126 mm glass fiber filters yield 10-15% higher results than the glass fiber hi-vol, quartz and Fluoropore filters. Using the Brosset technique for the comparison, Fluoropore results are lower by about 10% relative to the 126 mm glass and quartz filters. However, the latter results include only sulfate on particles < 3.5 µm. Since "coarse" (i.e., > 3.5 µm) sulfate was below the detection limit of 1.5 $\mu g/m^3$, the error introduced by omitting large particle sulfate cannot be accurately assessed. Assuming a value of 0.8 $\mu g/m^3$ (i.e., one-half the detection limit) for coarse sulfate, this amount added to the fine Fluoropore results, would decrease the ratio of means quartz/total Fluoropore by the Brosset method to 1.04.

If this argument is valid, then Fluoropore results should also be too low by the MTB method. However, four of the Fluoropore samples included in this comparison were in the range 6.0-7.2 µg/ml sulfate, just at, and slightly below, the working range as determined in Section III. Positive errors are likely with these samples (see Figures 14-17). A quartz/Fluoropore ratio of 0.98 by the MTB method may reflect the combined influence of omission of coarse sulfate and the positive errors at low sulfate concentrations.

An important application of inter-filter comparisons is to determine the extent of artifact sulfate formation. However, the ratio 126 mm glass/quartz of 1.1 for the MTB method but 0.94-0.99 for the BC and Brosset techniques is not consistent with artifact formation as the cause. Such a source of added sulfate (or sulfite) would contribute about equally to the three methods. These observations are, however, consistent with the significance of analytical interferents; as shown in Table 46, the maximum error by the MTB method for the 126 mm glass fiber samples is 0.6 $\mu g/m^3$ greater than with the quartz samples. Furthermore, since silicate from the filter medium is the most significant single interferent with the glass fiber sample compared to phosphate from the particulate matter (which varies from day to day) for the quartz sample, the glass fiber results should, on average, be even greater than this 0.6 $\mu g/m^3$ difference would suggest. For example, subtracting 1.0 $\mu g/m^3$ from each 126 mm glass filter result would reduce the glass/quartz ratio from 1.12 to 1.03.

It is concluded that no clear evidence of artifact sulfate formation may be obtained by evaluating the present results of side-by-side sampling. However, such differences may be largely explained based upon estimated interference effects in the sulfate methods and analytical error for samples containing low sulfate levels. Since particle collection efficiencies have not been evaluated for the quartz filter, lower sulfate on these filters may also reflect this factor.

## Table 50

## COMPARISON OF MTB SULFATE VALUES FOR ST. LOUIS SAMPLES ON DIFFERENT FILTER MEDIA ($\mu g/m^3$)

| Sampling Day | Hi-Vol Glass | 126 mm Filter (Glass) | 126 mm Filter (Quartz) | Fine Fluoropore |
|---|---|---|---|---|
| | | **URBAN** | | |
| 1 | 7.0 ± .1 | 8.2 ± .1 | 7.6 ± .3 | (7.8)[a] |
| 2 | --- | 11.2 ± .1 | 9.7 ± .3 | 9.7 |
| 3 | --- | 23.9 ± .1 | 22.3 ± .5 | 20.6 |
| 4 | 23.4 ± .7 | 28.2 ± .2 | 27.4 ± .3 | 24.8 |
| 5 | 13.1 ± .1 | 15.9 ± .2 | 14.6 ± .4 | 14.2 |
| 6 | 6.8 ± .1 | 7.2 ± .03 | 6.0 ± .1 | (7.9) |
| 16 | 22.7 ± .3 | --- | 28.1 ± .4 | 28.5 |
| 18 | 12.6 ± .1 | --- | 14.9 ± .2 | 13.5 |
| 19 | 6.1 ± .2 | 7.6 ± .04 | 6.5 ± .1 | (7.8) 8.3 |
| | | **RURAL** | | |
| 1 | 3.2 ± .1 | 3.1 ± .1 | 2.7 ± .1 | (ca. 0) |
| 2 | 3.9 ± .1 | 3.9 ± .1 | 3.7 ± .1 | (7.2) |
| 3 | 24.6 ± .4 | 25.8 ± .2 | 24.9 ± .2 | 25.5 |
| 4 | 22.4 ± .6 | 25.0 ± .3 | 23.2 ± .2 | 23.0 |
| 5 | 9.7 ± .1 | 10.8 ± .03 | 10.1 ± .1 | 11.1 |
| 6 | 4.8 ± .1 | 5.1 ± .1 | 4.5 ± .2 | (7.2) |
| 10 | 11.1 ± .1 | 13.8 ± .1 | 10.4 ± .1 | 12.0 |
| 11 | 12.6 ± .1 | 15.7 ± .1 | 12.1 ± .1 | 12.6 |
| 12 | 4.8 ± .2 | 5.1 ± .1 | 5.1 ± .2 | (7.6) |
| 19 | 8.3 ± .1 | 11.2 ± .1 | 8.0 ± .2 | 9.94 |

**Ratio of means:** 126 mm glass filter/glass hi-vol = 1.15[b],
126 mm glass filter/quartz filter = 1.12[c]
126 mm glass filter/fine Fluoropore = 1.10[c,d]
126 mm quartz filter/fine Fluoropore = 0.98[d]
Hi-vol (glass)/fine Fluoropore = 0.91

---

[a] Values in parentheses result from concentrations below 6 μg/ml and are probably too high.

[b] Excludes days 2, 3, 16 and 18, urban samples.

[c] Excludes days 16 and 18, urban samples.

[d] Excludes values in parentheses.

## TABLE 51

## COMPARISON OF MODIFIED BROSSET SULFATE VALUES FOR ST. LOUIS SAMPLES ON DIFFERENT FILTER MEDIA ($\mu g/m^3$)

| Sampling Day | 126 mm Filter Glass | 126 mm Filter Quartz | "Fine" Fluoropore |
|---|---|---|---|
| | | **URBAN** | |
| 1 | 7.1 ± .6 | 8.0 ± .2 | 3.8 |
| 2 | 11.9 ± 1.8 | 10.6 ± .3 | 8.3 |
| 3 | 21.3 ± 1.7 | 23.2 ± 1.0 | 20.2 |
| 4 | 25.5 ± 2.4 | 27.7 ± .2 | 26.4 |
| 5 | 14.5 ± .3 | 15.4 ± .4 | 13.5 |
| 6 | 6.5 ± .3 | 6.3 ± .1 | 4.5 |
| 16 | | 29.2 ± .4 | 30.3 |
| 18 | | 15.8 ± .2 | 11.9 |
| 19 | 6.9 ± .2 | 6.9 ± .3 | 4.8 ± .2 |
| | | **RURAL** | |
| 1 | 1.2 ± .1 | 1.5 ± .3 | <1.6 |
| 2 | 2.0 ± .3 | 3.1 ± .3 | 2.6 |
| 3 | 23.1 ± 1.6 | 24.4 ± .7 | 25.4 |
| 4 | 22.0 ± 2.0 | 22.5 ± 1.3 | 22.8 |
| 5 | 9.9 ± .2 | 10.2 ± .4 | 8.8 |
| 6 | 3.8 ± .1 | 3.9 ± .1 | 3.5 |
| 10 | 12.5 ± .4 | 11.0 ± 1.8 | 9.5 |
| 11 | 14.4 ± .4 | 11.7 ± .3 | 10.9 |
| 12 | 3.7 ± .3 | 4.4 ± .1 | 3.4 |
| 19 | 9.9 ± .5 | 8.0 ± .1 | 6.9 |

Ratio of means glass/quartz = 0.99 ± .03[a]
glass/fine Fluoropore = 1.1[a]
quartz/fine Fluoropore = 1.1

[a] Excludes day 16 and 18, urban samples.

## TABLE 52

## COMPARISON OF BC SULFATE VALUES FOR ST. LOUIS SAMPLES ON DIFFERENT FILTER MEDIA ($\mu g/m^3$)

| Sampling Day | Hi-Vol Glass | 126 mm Filter (Glass) | 126 mm Filter (Quartz) | Fine Fluoropore |
|---|---|---|---|---|
| | | **URBAN** | | |
| 1 | 7.3 ± .2 | 7.0 ± .3 | 11.6 ± .3 | 5.1 |
| 2 | - | | 9.3 ± .6 | 8.2 |
| 3 | - | 19.0 ± 1.4 | 22.2 ± 1.6 | 11.9 |
| 4 | 22.8 ± .9 | | | 23.9 |
| 5 | 13.0 ± .4 | 12.4 ± 1.5 | | 5.6 |
| 6 | 6.7 ± .4 | 5.4 ± .3 | 5.9 ± .1 | < 4.8 |
| 16 | 21.6 ± .5 | | 25.6 ± 1.8 | 27.4 |
| 18 | 12.6 ± .5 | | 15.1 ± .9 | 14.8 |
| 19 | 6.5 ± .2 | | | 5.7 (<4.8) |
| | | **RURAL** | | |
| 1 | 3.5 ± .3 | | | < 5.1 |
| 2 | 4.1 ± .3 | | 3.8 ± .3 | < 4.8 |
| 3 | 22.6 ± .8 | 23.8 ± 1.2 | | 25.1 |
| 4 | 21.6 ± 1.3 | 22.6 ± .4 | 21.0 ± .5 | 18.7 |
| 5 | 10.2 ± .1 | 7.9 ± .02 | 10.6 ± .5 | 5.8 |
| 6 | 5.3 ± .2 | | 4.2 ± .4 | < 4.6 |
| 10 | 11.1 ± .5 | | 9.2 ± .5 | < 4.8 |
| 11 | 12.9 ± .6 | 12.9 ± .5 | 10.5 ± .5 | 10.2 |
| 12 | 5.2 ± .2 | | 3.9 ± .8 | < 4.7 |
| 19 | 9.1 ± .3 | 9.0 ± 1.0 | 7.2 ± .1 | 15.6 |

126 mm glass / hi-vol (glass) = 0.98[b]
126 mm glass / 126 mm quartz = 0.94[b]
quartz / Fine Fluoropore = 1.1[a,b]
hi-vol (glass) / Fine Fluoropore = 1.0[a]

a. The poor agreement between BC and Brosset results for the fine Fluoropore samples suggests the BC values are suspect. Little credence is given to these ratios.

b. Ratio of means based on 9 sampling days.

Table 55

## STATISTICAL EVALUATION OF MEAN DIFFERENCES IN SULFATE RESULTS ON DIFFERENT FILTER MEDIA BY THE BC METHOD

| Filter Media Compared | No. of Samples | Mean Diff. ($\mu g/m^3$) | 95% Conf. Interv. | Significance[a] of Difference |
|---|---|---|---|---|
| 126 glass/hi-vol glass | 5 | .34 | ± 1.50 | p = .83 |
| 126 glass/126 mm quartz | 5 | .30 | ± 3.90 | p = .71 |
| 126 mm quartz/fine Fluoropore | 5 | 1.10 | ± 7.22 | p = .79 |
| Hi-vol glass/fine Fluoropore | 5 | 1.14 | ± 5.40 | p = .79 |

a. By the Wilcoxon signed rank test.

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## Appendix A

## DIFFERENCES IN EPA AND AIHL LABORATORY PROCEDURES FOR THE AUTO TECHNICON II MTB SULFATE METHOD*

1. Principle and Applicability

1.1 A linear regression fit of the working curve from 5-60 μg/ml was employed for data reduction except where noted.

2. Range and Sensitivity

2.1 Using linear regression, the working range of the MTB Method was determined to be 7-75 μg/ml on atmospheric extracts with an accuracy of ± 5% relative to the accuracy in the optimal range of the method.

5. Apparatus

5.2.1.1 A Technicon Auto Analyzer Sampler IV with a 30 sample/hr. cam having a 6:1 sample to wash time ratio was used.

5.2.1.4 Ion - Exchange Column: A small piece of stainless steel mesh was used as plugs at the ends of the ion-exchange column instead of glass wool.

5.2.1.7 Linearizer: No linearizer was employed.

5.2.1.8 A single channel Recorder was used.

5.2.1.9 Modular Digital Printer: Not provided.

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*Section numbers used here are taken from the EMSL/RTP Draft Auto-Technicon II Procedure, 9/19/75.

5.2.1.10 Pump tubing: The tubing used was as given in the EMSL procedure with the exception of the pump tube from the sample probe which was flowrated at 0.42 ml/min instead of 0.32 ml/min.

6. Reagents (The AIHL procedures followed those given by Technicon Industrial Method 226-72W)

6.2.12 Sodium Hydroxide solution 0.18 N instead of 0.08N.
Dissolve 7.2 g of sodium hydroxide in distilled water and make to 1000 ml in volumetric flask.

6.2.13 Hydrochloric Acid 10.0 N instead of 1.0N.
Add 83 ml of concentrated hydrochloric acid to water in volumetric flask and make to 100 ml.

6.2.14 Barium Chloride - Hydrochloric Acid Stock.
Solution: Add 16 ml of 10N HCl and 1.526 g $BaCl_2 2H_2O$ to a volumetric flask and make up to 1000 ml with distilled water.

6.2.15 Methylthymol Blue Solution:
To 0.1182 g instead of 0.1352 g of MTB in a 500-ml volumetric flask, add successively 25 ml of stock solution from 6.2.14, 75 ml of distilled water and make to 500 ml with 95% ethanol. Prepare fresh daily.

6.2.18 Stock sulfate solution (1000 $\mu g\ SO_4^{-2}/ml$). Dissolve 1.479 g anhydrous sodium sulfate in a volumetric flask and make up to 1000 ml with distilled water.

6.2.19 Blank Reagent Color Solution: Not prepared.

6.2.20 Potassium Chloride Solution: Not prepared.

## 7. Procedure

### 7.2.2.1 General:

The sample turntable rate used was 30 samples per hour with a 6:1 sample to wash time ratio.

### 7.2.2.2 Sample and Quality Control Standard Loading:

For all standard sulfate solutions and atmospheric extracts, two cups of solution are analyzed in sequence and only the second cup value is considered valid. This protocol minimizes the analytical error (memory effect) which occurs when successive samples differ greatly in sulfate concentration ($\Delta \geq 20$ μg/ml). Each day before the analysis of atmospheric samples, standard solutions of 60, 50, 40, 30, 20, 10, 5 μg/ml are analyzed and the working curve compared with a historical data base for linearity as a quality control measure. Standards are interspersed with the atmospheric samples such that each sample set (15-20 filter extracts) can be reduced with a separate calibration curve encompassing the range 5-60 μg/ml $SO_4^{-2}$. This compensates for the small drift in the baseline (1%/4 hrs.). No correction is made for highly-colored sample extracts because preliminary results suggest a maximum interference of 2% from this source.

### 7.2.3. System Maintenance:

The sample manifold was equipped with a column by-pass valve which removes the ion-exchange column from the flow circuit during washing (see figure) and permits removal of air bubbles during the start-up operation.

8. Calibration

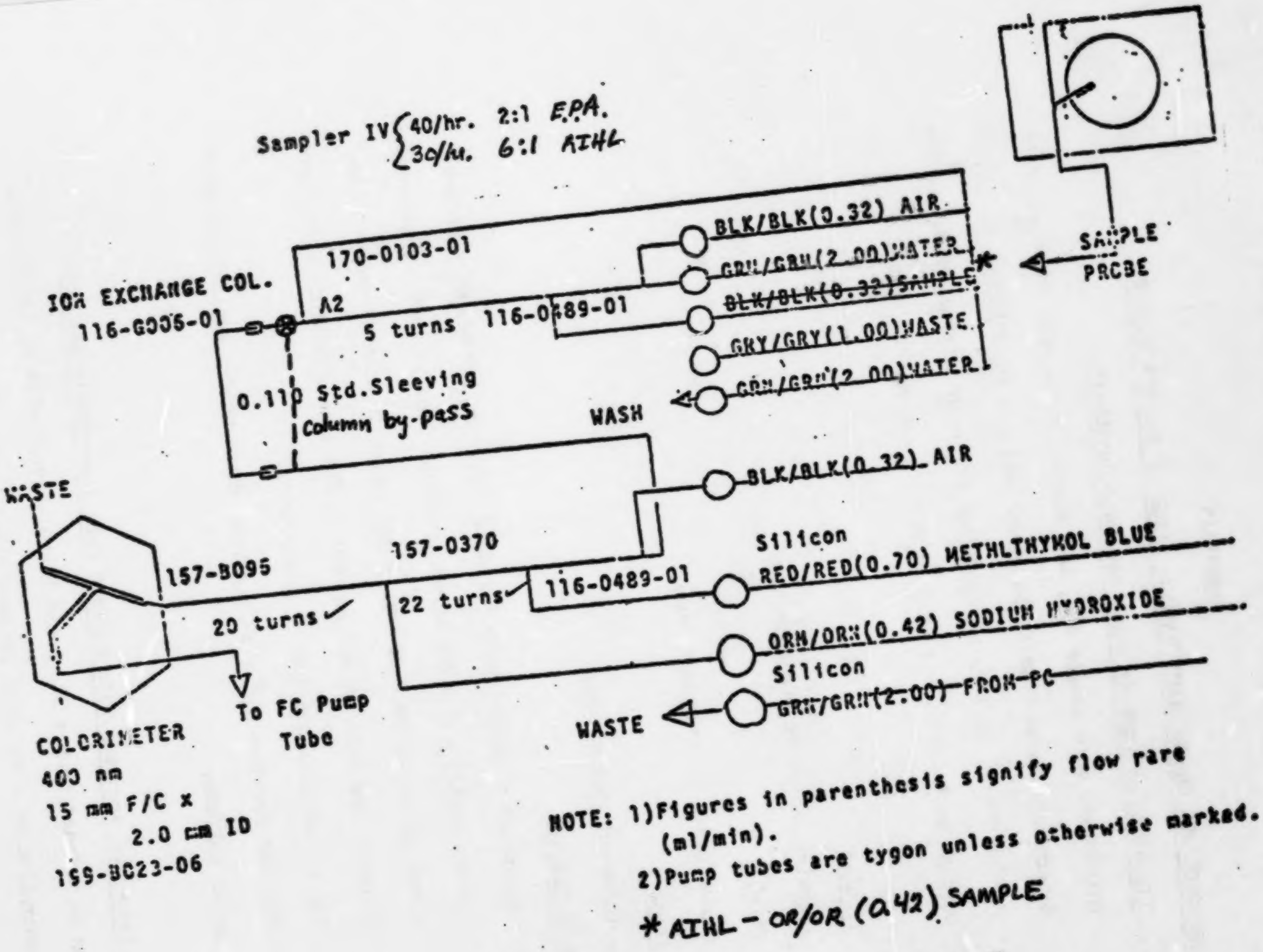
8.2.1 Flow Rates: Degradation in flowrated pump tubing is monitored daily by evaluation of the calibration curve per 7.2.2.2.

8.2.3 Concentration Standards: Transfer about 50 ml of the 1000 μg/ml standard sulfate solution into a smaller container which allows easy access with a digital pipet. With a 5 ml digital pipet, transfer the following volumes of the 1000 μg/ml standard into 100 ml volumetric flasks and fill to the mark with distilled water:

| Standard μg/ml (100 ml Volumetric) | mls of 1000 μg/ml Stock |
|---|---|
| 5 | 0.5 |
| 10 | 1.0 |
| 20 | 2.0 |
| 30 | 3.0 |
| 40 | 4.0 |
| 50 | 5.0 |
| 60 | 6.0 |

8.2.6 Baseline Adjustment: No baseline adjustment is performed since standards are interspersed with the samples.

8.2.7 Calibration Standards: The set of standards run at the beginning of the day is compared with the standards interspersed in each sample set of the day. If the variation between sets of standards is more than 3 μg/ml, that run is considered invalid and must be repeated.


Sampler IV { 40/hr. 2:1 E.P.A.
30/hr. 6:1 AIHL
SAMPLE PROBE
170-0103-01
ION EXCHANGE COL.
116-G005-01
A2
5 turns
116-0489-01
0.110 Std.Sleeving
Column by-pass
BLK/BLK(0.32) AIR
GRN/GRN(2.00)WATER
*
BLK/BLK(0.32)SAMPLE
GRY/GRY(1.00)WASTE
GRN/GRN(2.00)WATER
WASH
BLK/BLK(0.32) AIR
WASTE
157-0370
157-B095
Silicon
RED/RED(0.70) METHLTHYMOL BLUE
22 turns
116-0489-01
20 turns
ORN/ORN(0.42) SODIUM HYDROXIDE
Silicon
GRN/GRN(2.00) FROM FC
To FC Pump Tube
WASTE
COLORIMETER
400 nm
15 mm F/C x
2.0 mm ID
199-B023-06

NOTE: 1)Figures in parenthesis signify flow rare
(ml/min).
2)Pump tubes are tygon unless otherwise marked.

* AIHL - OR/OR (0.42) SAMPLE

Figure A-1. Sulfate in water and waste water (range 0-100 μg/ml $SO_4^=$.

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## Appendix B

## PROTOCOL FOR DETERMINING WORKING RANGE OF THE MTB METHOD

### 1. Linearity of working curve and reproducibility

Determine, on a single day, the working curve with three separate determinations each with the concentrations 75, 70, 65, 60, 50, 40, 30, 20, 10, 8, 6, 4 μg/ml sulfate. For each determination use two cups at each level, but only report the second cup value.

**Trial A**

stepwise change in concentration

**Trial B**

random order of concentrations

**Trial C**

a different random order

**Data Display**

A. Construct a single curve plotting the mean instrument response (chart units) ± 2 σ for three determinations at each concentration level listed above. Determine the range in concentration which provides the best linear regression fit as a function of scatter (Sy.x) and plot the least squares line.

B. Plot the variance ($\sigma^2$), in recorder chart units, against the true μg/ml sulfate.

### 2. Precision and accuracy with sulfate from atmospheric samples

Using an extract from a St. Louis Hi-vol sample with an initial $SO_4^=$ concentration of ≥ 85 μg/ml prepare dilutions at the same concentrations shown in (1). Analyze with three determinations using separate working curves. Determine mean and $\sigma$ for each determination in μg/ml employing a linear regression fit of the working curve. Assume that the calculated undiluted concentration previously obtained from analysis of the hi-vol extract in the optimal range of the method (ca. 35 μg/ml) is the "expected" concentration. Calculate the ratios observed/expected concentrations.

All analyses are performed by the same chemist.

## Data Display

A. Plot observed/expected concentration as a function of the μg/ml when analyzed.

B. Plot the variance calculated for the diluted solutions against the observed μg/ml when analyzed.

## Appendix C

## The Modified[*] Brosset Method for Sulfate Analysis[1,2]

1. Principle

1.1 Aqueous extracts of particulate matter are freed from cationic interferences by contacting the solution with a strong acid ion exchange resin. Sulfates are converted into sulfuric acid.

1.2 The dilute sulfuric acid solutions are mixed with an alcoholic solution containing excess barium. Sulfuric acid reacts with barium which precipitates as insoluble $BaSO_4$.

1.3 Excess barium is reacted with Thorin $(2\text{-}(OH)_2AsOC_6H_4N{:}N\text{-}1\text{-}C_{10}H_4\text{-}2\text{-}OH\text{-}3,6\text{-}(SO_3Na)_2)$ and the colloidal complex is measured at 520 nm in a spectrophotometer.

2. Range and Sensitivity

2.1 The concentrations of the reagents are selected to cover a range from 0 to 12 μg/ml. The useful range is approximately 3 to 10 μg/ml.[**]

2.2 The limit of detection is about 0.03 μg/ml.

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[*] Modifications based upon procedures employed by Dr. J. Stikeleather, Northrup Service, under contract to the EPA.

[**] The working range, defined as the region of constant variance, is to be evaluated as part of the present AIHL study.

## 3. Interferences

3.1 Cationic interferences in solution are eliminated with the ion exchange treatment. However some cations like Ba, Sr, Ca, Fe, Pb may react with sulfate prior to ion exchange, thus producing a negative interference. The interference for the elements listed, except Ba, was found to be less than 5% for sulfate:interferent ratios of 2:1 w/w and 0.7:1 w/w when using acetone as solvent.***

3.2 Anionic interferents, such as phosphate, may react with the barium thus producing a negative interference. The interference was found to be less than 10% under the conditions given in 3.1.

3.3 Colloidal clay and a yellow organic material caused generally less than a 10% interference effect when using acetone as the solvent.

## 4. Precision and Accuracy

4.1 Under careful conditions the reproducibility of the method is within ± 0.2 μg/ml.

4.2 The accuracy of the method in isopropyl alcohol was evaluated with aqueous extracts of filter strips loaded with known quantities of $K_2SO_4$. On average the results differed by 1% from those reported by EPA. The accuracy of the method using extracts from atmospheric samples has not been evaluated with this solvent. In acetone, recoveries of sulfate were typically 100-110% with standard additions to atmospheric particulate extracts. However such recoveries may not correlate with those attainable from atmospheric samples.

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***Interference effects using isopropyl alcohol as solvent are being evaluated as part of the present AIHL study.

## 5. Apparatus

5.1 Ion exchange columns 200 mm long and 5 to 6 mm in diameter or similar such as those described in AOAC 6th Ed. 1945, p. 609 available from Kontes as Chromaflex columns cat. no. K420150.

5.2 Automatic pipet. Consists of a three syringe system, operated pneumatically on a two cycle loading and unloading sequence. The cycles are triggered by a foot operated air release valve. Each syringe has a stop on its upper portion which can be set with an hexagonal Allen wrench after releasing the lock pin which holds the stop in place. The setting screw is barreled and has four vernier divisions, each of which corresponds to 0.1 ml. One syringe, the sample syringe, pulls liquid from a tip through a long tubing which holds the sample solution. The second cycle pushes the sample through the same sample inflow opening. The second syringe, pulls the diluent out of a container and empties it into the sample syringe, thus flushing its content through the same tubing as the sample and pushes its content through the same sample inflow opening. The third syringe is independent and pulls the Thorin reagent solution out of a container and then pushes it through a separate delivering port. Both delivery ports are positioned together, which allows a simultaneous delivery into a single spectrophotometric cell.

5.3 Spectrophotometric cells. Square 20 mm cells are preferable if adapters for the spectrophotometers are available. Cylindrical 25 mm pathlength cells can be used, provided that they are kept clean and free of bubbles.

5.4 Spectrophotometer. 2 nm slit width with output for recorder or voltmeter.

5.5 Digital Voltmeter. 5-1/2 digits, capable of reading the absorbance output of the spectrophotometer such as Fluke Model 8800 A.

## 6. Reagents

6.1 Air or Nitrogen. The Autopipet requires 65 ± 5 psi air pressure. If not available from the laboratory compressed air line, cylinder air or nitrogen may be used.

6.2 Distilled water. Water distilled from a very dilute $KMnO_4$ solution in an all glass system is preferable.

6.3 Perchloric acid, 0.1 M, as alternate to distilled $H_2O$ for extracting sulfate from particulate samples.

6.4 Ion exchange resin. Type Dowex 50W X8 hydrogen form 50-100 mesh or equivalent such as BioRad AG 50W X8 hydrogen form 50-100 mesh.

6.5 Sulfate stock, 1000 ppm $SO_4^=$. Dilute 10.42 ml of commercial 1 N $H_2SO_4$ to 500 ml with distilled water ( solution is 0.0104 M $H_2SO_4$).

6.6 Barium stock. Dissolve 550 mg anhydrous $Ba(ClO_4)_2$ in 6 ml 72% $HClO_4$ and fill to 250 ml with distilled water.

6.7 Diluent. Take 10 ml of barium stock and fill to 1 liter with isopropanol.

6.8 Thorin reagent. Dissolve 200 mg Thorin in 7 ml 0.01 N $H_2SO_4$ (or 3.5 ml sulfate stock, 1000 ppm $SO_4^=$) and fill to 250 ml with distilled water. This solution is stable for four weeks if stored in a brown bottle.

## 7. Procedure

7.1 The extraction technique varies with the sample size. Either distilled water or 0.1 M $HClO_4$ may be used. References 3 and 4 discuss extraction methods. Depending on the extraction technique, extracts may be filtered after cooling.

7.2 Ion exchange treatment.

7.2.1 Resin preparation. Stir resin into water in a beaker. Discard the fines by decanting several times. Soak for one or two hours and renew the water a few times. Then let soak overnight and fill the columns.

7.2.2 Column preparation. Fill ion exchange columns to 12-13 cm height with resin. The tip of the column is plugged from the inside with a small glass wool swab before filling the resin. Attach a piece of rubber tubing and a pinch-off clamp to the tip for flow control. Fill with aid of a Pasteur pipet slurrying the resin in a beaker. Avoid air entrapment. Flush the columns with distilled water before use and keep covered with water. If air gets entrapped, re-make the column, flush water from the tip up to the reservoir, or stir with a Pasteur pipet containing water from the top down. Cover with a plastic foil. Renew the columns after 20 cycles.

7.2.3 Procedure. Drain off the distilled water from the reservoir through the column. Add 10 ml fresh distilled water and flush through. Just before air reaches the top of the resin bed, add 5 ml of sample extract. Discard this first portion and add a second 5 ml portion of the sample extract. Collect this fraction in a 25 ml beaker or Erlenmeyer. Cover after collection. Flush the column with 10 ml of distilled water before using it for a new sample. For storage, flush with about 10 ml distilled water, then fill the reservoir, pinch-off the flow and cover with a plastic foil.

7.3 Analysis

7.3.1 Operation of the automatic pipet (see 5.3)

The syringe delivering the sample is set at 1.8 ml.

The syringe delivering the diluent is set at 4.8 ml.

The syringe delivering the Thorin reagent is set at 0.4 ml.

Total volume = 7.0 ml.

The volume of 7 ml is equal to the capacity of the 25 mm pathlength cylindrical cell and can also be used with the 20 mm square cells. If other volumes are necessary or desired, the formulations of the individual reagent solutions must be modified accordingly. Proportional amounts of Ba, Thorin and sulfate, as well as the same ratio of water to alcohol must be maintained.

7.3.2 Adjustment of the spectrophotometer.

When using a double beam instrument, one beam must be balanced by inserting a grey wedge, filter or solution, at the operational wavelength, i.e. 520 nm.

7.3.3 Zeroing of the spectrophotometer. Operate the filling mechanism of the automatic pipet first using distilled water a few times, until stabilized. Set the digital voltmeter to read 0.800 absorbance units. With intervals of 5 minutes make several blank measurements, and record the readings. Drifting should be less than 0.5% or 0.004.

7.3.4 Measurement procedure. Submerge the syringe port tubing into the sample beaker. Press foot pedal and wait until the sample is pulled into the long holding plastic tube. Withdraw the beaker and place the cell under the syringe port tubings. Press foot pedal and wait until all the three syringes have delivered their contents. Cap well, shake to free bubbles, insert in spectrophotometer, wait until stabilized and read at 520 nm.

7.3.5 Measurement. Samples are run with two determinations within the working range of the method. If the initial value exceeds the range, use twofold dilutions using a repetitive pipet and repeat the measurements. If dilutions of the extracts are necessary these should be made following the ion exchange treatment. Continue diluting until readings fall in the working range.

## 8. Calibration

8.1 Standards. With a 1 ml repetitive pipet measure 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 ml of the 1000 ppm sulfate stock solution into 100 ml volumetric flasks and fill to mark.

8.2 Quality control.

8.2.1 After a days run, clean the quartz cell with alkaline acetone (one drop 5 M ammonia, a shot of acetone from a squeeze bottle), cap the cell and shake. Add a little water and continue shaking, then rinse a few times and drain. An orange deposit may form occasionally which is a Ba-Thorin insoluble salt.

8.2.2 Run new standards in triplicate when making up fresh reagent, when changing solvents and every day before analyzing samples. Check the calibration line; points should be almost co-linear between 3 and 10 μg/ml if standards have been properly prepared and if spurious sulfate introduced by reagents is not excessive.

8.3 Calibration. Calibrate the instrument running standards in duplicate or triplicate within the range of 3 to 10 μg/ml. If desired, duplicates can be run before and after measuring sample solutions.

## 9. Calculation

9.1 Calculate a least square regression line with the data obtained by running the standard calibrating solutions. If standards are run both before and after the samples, pool all data for a single regression line.

9.2 Concentrations of the sample are calculated in μg/ml using the regression line obtained above.

9.3 Multiply the concentration values by the dilution factor in order to obtain original extract concentrations. Multiply these values by the extract volume to obtain the amount of sulfate extracted from the filter samples.

10. Storage effects. Sulfate standards and samples are stable for several weeks at room temperature, and up to a year if stored in a refrigerator and protected from light.

## 11. References

1. Brosset C and Ferm M: An improved spectrophotometric method for the determination of low sulfate concentrations in aqueous solutions. To be published in Atmospheric Environment.
2. Air Quality-sulfur dioxide concentrations in air- analysis by the thorin (spectrophotometric) method. International Organization for Normalization, 1974-05-15, ISO/TC 146/WG 1/TG 4N18.
3. Hoffer EM and Appel BR: A comparative study of extraction methods for sulfate and nitrate from atmospheric particulate matter. AIHL Report No. 181, Air and Industrial Hygiene Laboratory, California State Department of Health, November 1975.
4. Jutze GA and Foster KE: Recommended standard method for atmospheric sampling of fine particulate matter by filter media--high-volume sampler. JAPCA 17 17 (1967).

Appendix D

# BARIUM CHLORANILATE METHOD FOR DETERMINATION OF SULFATES IN THE ATMOSPHERE[a]

March 1976

U.S. Environmental Protection Agency
Environmental Monitoring and Support Laboratory
Research Triangle Park, North Carolina 27711

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[a] This method has been carefully drafted from available experimental information. The method is still under investigation and therefore, is subject to revisions.

# BARIUM CHLORANILATE METHOD FOR DETERMINATION OF SULFATES IN THE ATMOSPHERE

## 1. Principle and Applicability

1.1 Ambient sulfates are collected by drawing air through a glass fiber filter with a high-volume pump. The filters are extracted with water and the extract treated with excess barium chloranilate.(1,2) The released chloranilic acid equivalent to the sulfate content of the sample is then measured at a pH of 2.0(3) spectrophotometrically at 312 nm. If the absorbance is too high the absorbance may be measured at 530 nm without diluting the sample.

1.2 The method is applicable to the collection of 24-hr samples in the field and subsequent analysis in the laboratory.

## 2. Range and Sensitivity

2.1 The range of the analysis at 312 nm is 1 to 60 µg $SO_4^=$/ml. By using the 530 nm absorption peak, the range may be extended to 1,500 µg/ml. With a 50-ml extract from 1/12 of the exposed high volume filter collected at a sampling rate of 1.7 $m^3$/min (60 cfm) for 24 hr, the range of the method is 0.2 to 300 µg/$m^3$. The lower range may be extended up to 12-fold by increasing the portion of the filter extracted.

2.2 Using the procedure outlined, a concentration of 1.6 µg/ml will produce an absorbance of 0.02 at 312 nm.

## 3. Interferences

3.1 Water soluble chlorides, fluorides and phosphates produce a positive interference which is dependent on the concentrations.(3) Chloride at 20 times the sulfate concentration produces a positive error of ~ 10%. Fluorides produce only a slight interference except when present as fluosilicate. The absorbance produced by 50 µg of fluoride as fluosilicate is 0.03. The absorbance produced by 100 µg of phosphate is equal to 0.01.

3.2 The interferences from water soluble cations are removed by contacting the sample with a hydrogen form ion-exchange resin. Cations such as $Ca^{+2}$ or $Pb^{+2}$, which form insoluble sulfates and which are present in concentrations which exceed the solubility product of the respective compounds cause a negative interference.

## 4. Precision and Accuracy

4.1 A single laboratory's relative standard deviation for the analysis is 2.5%.(3) Overall precision is not presently known.

4.2 Adequate data for accuracy determinations is not presently available.

## 5. Apparatus

5.1 Sampling: Apparatus as specified in Appendix B - "Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method),"(4) shall be used.

### 5.2 Analysis

5.2.1 Spectrophotometer: Capable of measuring absorbance at 312 and 530 nm.

5.2.2 Spectrophotometer Cells: Matched set of cells with a 10 mm path length constructed of high silica material transparent in the ultraviolet to visible reagon (165 to 2,600 nm).

5.2.3 Filter Paper: Whatman No. 4 or equivalent 55 mm in diameter.

5.2.4 Filter Paper: Whatman No. 42 or equivalent 55 mm in diameter.

5.2.5 pH Meter: Capable of measuring the pH to nearest 0.1 pH units over a range of 0 to 14.

5.2.6 Mechanical Shaker: Capacity for shaking the required number of samples. For a small number of samples a magnetic stirrer may be used in place of the shaker.

5.2.7 Erlenmeyer Flask: 125 ml with 24/40\$ joint.

5.2.8 Condenser: Water jacketed, 300 mm length with \$ 24/40 joints.

5.2.9 Hot Plate: Suitable for sample extraction (7.21).

5.2.10 Volumetric Flasks: Class A - 50, 100, 500, 1,000 ml capacity.

5.2.11 Pipets: Class A-1, 5, 10, 20, 50 ml volumetric; 10 ml graduated in 1/10 ml intervals.

5.2.12 Buchner Funnels: Buchner style 150 ml capacity with fine-pore fritted glass filter.

5.2.13 Buchner Funnels: Buchner style with a perforated plate and 150 ml capacity for 55 mm filter paper.

5.2.14 Vacuum Filtering Apparatus: Device which permits vacuum filtering directly into receiver. This consists of a bell jar with a top opening, a side tubulation and a bottom plate. The Buchner funnel passes through the top opening and is sealed to the bell jar with a stopper. The bell jar should be tall enough to contain the graduated tubes used for collecting the samples. The vacuum connection is made using the side tubulation. The filtering apparatus is shown in Figure D-1.

5.2.15 Vacuum Pump: Any device which can maintain a vacuum of at least 64 cm of Hg. Mechanical pumps or water aspirators may be used.

5.2.16 Polythylene Bottles: Bottles with a capacity of 60 ml (2 oz) fitted with polyseal caps.

5.2.17 Standard Scoop: Spatula with small (1/8 x 1/2 in.) spoon on one end. Practice with barium chloranilate and an analytical balance so that one scoop of approximately 25 mg can be measured out.

## 6. Reagents

### 6.1 Sampling

6.1.1 Filter Media: Filter media as specified in Appendix B - "Reference Method for Determination of Suspended Particulates in the Atmosphere (High Volume Method),"(4) shall be used. Each lot of filter should be analyzed for background sulfate content and pH using a statistically valid sample from that lot.

6.1.1.1 Determination of Filter pH: Cut a 9-$in.^2$ (58 $cm^2$) section of a glass fiber filter with pizza cutter. Place the filter in a 125-ml Erlenmeyer flask. Add 15 ml of 0.05 M KCl and stopper the flask. Stir with a magnetic stirrer for 10 min at 60 RPM. Determine the pH of the extract.

Obtain the pH for a given lot of filters, and report the mean and standard deviation. pH has an effect on accuracy of the collection procedure. The optimal pH value of the filter extract is not presently known but pH information will be useful for historical purposes. Filters currently used in the National Air Sampling Network (NASN) have a pH of 9.74 ± 0.89.

6.1.1.2 Determination of Filter $SO_4$ Content: Measure the sulfate content of each lot of filters. Cut a 3 x 8 in. (7.6 x 20.3 cm) strip from each filter using a pizza cutter and a template. Follow the procedures for extraction and analysis given in Sections 7.2.1 and 7.2.2. Calculate the mean and standard deviation in µg $SO_4$/in.$^2$. The $SO_4$ content of glass fiber filters may vary significantly from lot to lot. A low $SO_4$ content is desirable, but it is more important that the value be constant within a given lot.

### 6.2 Analysis

6.2.1 Sodium Hydroxide: ACS Reagent Grade.

6.2.2 Barium Chloranilate: Trihydrate Reagent Grade. The material must be crystalline; the amorphorus material forms a colloidal suspension which is difficult to remove. The product supplied by J. T. Baker Chemical Company has been found acceptable.

6.2.3 Cation Exchange Resin: Dowex 50W-X8, hydrogen form, or equivalent, 300 to 850 µm (20 to 50 mesh). The resin should be stirred into distilled water and the fines discarded before they can settle. The resin should be in a fully swollen condition before use. After soaking, remove excess water by filtering with section and pressing between sheets of filter paper.

6.2.4 Isopropyl Alcohol: ACS Reagent Grade.

6.2.5 Chloroacetic Acid: Minimum purity 99%; m.p. 61 to 62°C.

6.2.6 Sodium Sulfate: ACS Reagent Grade, anhydrous.

6.2.7 Potassium Chloride: ACS Reagent Grade.

6.2.8 Sodium Hydroxide Solution (1.0 N): Dissolve 20.0 g of sodium hydroxide in distilled water and make to 500 ml in a volumetric flask, transfer to a polyethylene bottle.

6.2.9 Buffer, pH 2.0: Dissolve 18.9 g of chloroacetic acid in 50 ml of distilled water. Adjust the pH to 2.0 by adding 1.0 N sodium hydroxide solution. Make the solution to 100 ml and recheck the pH.

6.2.10 Stock Sulfate Solution (1,000 µg $SO_4^{=}$/ml): Dissolve 1.4789 g of sodium sulfate ($Na_2SO_4$), which has been heated at 105°C for a minimum of 4 hr and cooled in a desiccator over anhydrous magnesium perchlorate, and dilute to 1,000 ml with distilled water. Store under refrigeration.

6.2.11 Distilled Water: ACS Reagent Grade, having a specific conductance of 2 microhms or less.

6.2.12 Potassium Chloride Solution (0.05 M): Dissolve 3.7 g of KCl in 1,000 ml of $CO_2$ free distilled water. The pH of this solution should be 7.0 ± 0.3.

## 7. Procedure

7.1 Sampling: Sampling procedure as specified in Appendix B - "Reference Method for the Determination of Suspended Particulate in the Atmosphere (High Volume Method),"(4) shall be used. Quality Assurance Guidelines for use with the High Volume Method are applicable to the collection of samples for sulfate determination.(5)

### 7.2 Analysis

7.2.1 Sample Extraction: Remove the filter from the folder, open flat, and cut a 3/4 x 8 in. (1.9 x 20.3 cm) strip using a pizza cutter and filter cutting template. The filter should be cut with the particulates face up. The filter strip is folded and placed in a 125 ml Erlenmeyer flask. Add 35 ml of distilled water to the flask and connect to a 300 mm water jacketed condenser. Place the flask condenser assembly on a hot plate and boil gently for 30 min. Maintain cold water circulation through the condenser while the sample cools to room temperature. Rinse the walls of the condenser with 5 ml of distilled water and disconnect the flask. Decant the liquid in the flask directly into the Buchner funnel of the filtering apparatus and filter into a glass graduated tube with a 50 ml graduation mark. Rinse the filter in the flask with a 5 ml portion of distilled water and add the rinse to the funnel. Squeeze the filter with a glass rod to remove the remaining extract and collect the filtrate. Repeat the rinse with a second 5 ml portion of distilled water. Collect the filtrate and dilute to a volume of 50 ml with distilled water. Transfer the sample to a 60 ml (2 oz) polyethylene bottle and cap with a polyseal cap. Mix thoroughly. These samples are stable at room temperature for at least 2 weeks.

A random 5 to 10% of the filters should be extracted in duplicate for purposes of qualifying the precision of measurement.

7.2.2 Sample Analysis: Transfer 20 ml of the sample to a 60 ml plastic bottle and add 1.5 g of ion exchange resin. Prepare a reagent blank in the same manner using 20 ml of distilled water. Seal the bottle with a polyseal cap and agitate for 15 min using either a mechanical shaker or magnetic stirrer. Vacuum filter the mixture using a Whatman No. 4 or equivalent filter paper. Do not wash. Pipet a 2-ml aliquot of the supernatant solution into a 60 ml plastic bottle containing 16 ml of isopropyl alcohol and mix. Transfer a fraction of the solution to the spectrophotometer cell and measure the absorbance at 312 nm against 80% isopropyl alcohol. Record the absorbance as the sample blank. Add one scoop of barium chloranilate to the solution remaining in the plastic bottle, seal the bottle and agitate mechanically for 15 min. Vacuum filter the mixture using a Whatman No. 42 or equivalent filter paper. Add 2 ml of buffer, mix and transfer the solutions to the spectrophotometer cell and measure the absorbance at 312 nm against 80% isopropyl alcohol. If the absorbance is too high for practical measurement at this wavelength, read at 530 nm. The amount of barium chloranilate specified is sufficient for samples containing up to 400 µg $SO_4^=$/ml.

## 8. Calibration

8.1 High Volume Sampler: The high volume air samplers shall be calibrated as specified in Appendix B - "Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)."(4)

8.2 Calibration Curve: Dilute 50.0 ml of stock sulfate solution containing 1,000 µg $SO_4^=$/ml to 500 ml with distilled water. This intermediate sulfate solution contains 100 µg $SO_4^=$/ml. Pipet 5, 10, 10, 15, 20, 50, and 60 ml of the 100 µg $SO_4^=$/ml solution into 100, 100, 50, 50, 50, 100, and 100 ml volumetric flasks and dilute to the mark with distilled water. These solutions contain 5, 10, 20, 30, 40, 50, and 60 µg $SO_4^=$/ml, respectively.

If samples contain sulfate concentration greater than 60 µg/ml, analysis is possible (without dilution) by measuring at 530 nm. This will require preparing a calibration curve for the 530 wavelength. Pipet 5, 10, 10, 15, 20, 50, and 50 ml of the 1,000 µg $SO_4^=$/ml stock solutions into 100, 100, 50, 50, 50, 100, and 100 ml volumetric flask and dilute to the mark with distilled water. These solutions contain 50, 100, 200, 300, 400, 500, and 600 µg $SO_4^=$/ml respectively.

Pipet 2 ml of the standard to a test tube and add 16 ml of isopropyl alcohol and one scoop of barium chloranilate. Agitate mechanically for 15 min and vacuum filter using a Whatman No. 42 or equivalent filter paper. A blank consisting of 2 ml of distilled water should be included with the calibration series. Add 2 ml of buffer, mix and transfer the solution to a 1 cm cell and read the absorbance at 312 nm against 80% isopropyl alcohol. Subtract the blank absorbance from the standard absorbance and plot net absorbance versus µg $SO_4^=$/ml. A straight line with a slope of 0.29 ± 0.1 absorbance units/µg $SO_4^=$/ml, passing through the origin, should be obtained.

## 9. Calculations

**9.1** Air Volume: The volume of air sampled shall be calculated according to Section (9.2.2) of Reference (3).

**9.2** Sulfate Concentration: Add the absorbance of the reagent blank and the sample blank and subtract from the absorbance of the sample. Using the calibration curve from 8.2, calculate the net μg $SO_4^=$ in the sample as follows:

### 9.2.1 μg $SO_4^=$ From Sample Extract (7.2.1)

$$\mu g\ SO^=_{4(S)} = \mu g\ SO_4^=/ml \times 50\ ml$$

where

μg $SO^=_{4(S)}$ = micrograms of sulfate in the sample extract

μg $SO_4^=$/ml = analyzed micrograms of sulfate from sample (7.2.2)

50 ml = total volume of extract

### 9.2.2 μg $SO_4^=$ From Filter Content (6.1.1.2)

$$\mu g\ SO^=_{4(F)} = \mu g\ SO_4^=\ m^2 - \text{filter} \times in^2 - \text{filter used}$$

where

μg $SO^=_{4(F)}$ = micrograms of sulfate from filter

μg $SO_4^=/in^2$ - filter = micrograms of sulfate in each square inch of filter (6.1.1.2)

$in^2$ filter used = square inches of filter used for the analysis, usually 6 (3/4 in. x 8 in.)

### 9.3 Calculate Concentration of Ambient Sulfates

where

$$C = \frac{12\,N}{V}$$

C = concentration of ambient sulfates, $\mu g/m^3$

12 = total width of exposed filter ÷ width of strip used (9 in. ÷ 3/4 in.)

N = net $\mu g$ $SO_4^{=}$, $\mu g$ from (9.2)

V = total volume sampled, $m^3$ from (9.1)

## 10. References

1. Bertolacini, R. J., and J. E. Barney, II, "Colorimetric Determination of Sulfate with Barium Chloranilate," Anal. Chem., 29:281-283 (1957).
2. Bertolacini, R. J., and J. E. Barney, II, "Ultraviolet Spectrophotometric Determination of Sulfate, Chloride, and Fluoride with Chloranilic Acid," Anal. Chem., 30:202-205 (1958).
3. Schafer, H. N. S., "An Improved Spectrophotometric Method for the Determination of Sulfate with Barium Chloranilate as Applied to Coal Ash and Related Materials," Anal. Chem., 39:1719-1726 (1967).
4. Appendix B - "Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," Federal Register, 36(84):8191-8194, April 30, 1971.
5. "Guidelines for Development of a Quality Assurance Program - Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method," EPA Environmental Monitoring Series, EPA-R4-73-028b, June 1973.

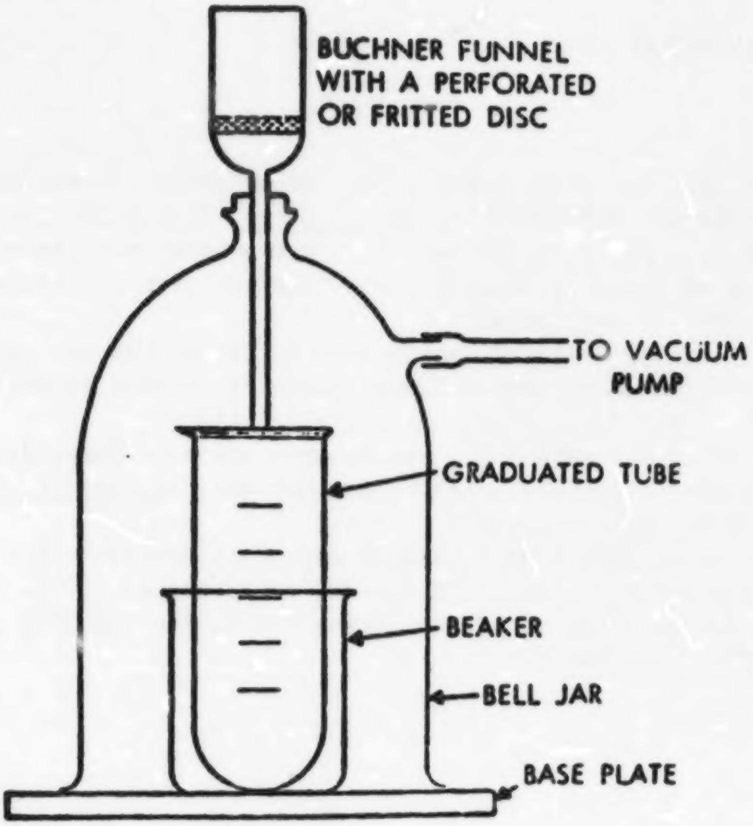
BUCHNER FUNNEL
WITH A PERFORATED
OR FRITTED DISC
TO VACUUM
PUMP
GRADUATED TUBE
BEAKER
BELL JAR
BASE PLATE

Figure D-1 Vacuum filtering apparatus.

# Appendix E

## AIHL Procedure for the EPA-MRI Barium Chloranilate Method

1. Transfer 20 ml of each sample or standard solution (standards cover the range between 6 and 60 μg/ml) and a convenient number of water zeroes (generally three) into 2 oz. plastic containers. Add one scoop (about 1.5 g) of prewashed, slightly damp ion exchange resin to each container, cap and shake on a shaker for 20 minutes.
2. Take 2 ml of the supernatant and place in a new set of 2 oz. plastic containers containing 16 ml of isopropyl alcohol. The alcohol is delivered from a repetitive pipet shortly before (no solution should be stored in the containers for more than four hours).
3. Measure the blank value of the mixture of sample plus alcohol at 312 nm. Return the liquid from the measuring cell back into the container.
4. Add a scoopful (about 15-20 mg) of barium chloranilate to the containers with the alcoholic solution. Put on a shaker for 20 minutes.
5. Filter a portion (about one-third) through a fine frit funnel unwashed from the previous sample. Discard. Pour in remainder and collect. Measure 9 ml from the filtrate with a glass pipet. Scrape and rinse the funnel with IPA after every four solutions.
6. Put the 9 ml in a glass tube containing 1 ml of buffer, mix and measure absorbance at 312 nm in the same spectrophotometric cell used above for blanks. Do all measurements against distilled water in the reference beam.
7. Deduct all blank readings from the corresponding sample, standard or zero readings.
8. Construct a calibration curve including the three values for the zero and calculate the least squares line. Calculate concentrations with slope and intercept for each day's run.

APPENDIX F

## Determination of Reactive Silicate[☆]

Reactive silicates are those forms of silicate which react with molybdic acid to give the silicomolybdate complex. Generally, only monomeric or dimeric silicates react whereas higher polymers do not. Silicates easily depolymerize at higher pH. Since glass fiber filters are believed to be the dominant source of silicate in the current program, and these are made out of relatively alkaline compositions, it is assumed that most of the soluble silicate in the extracts is reactive.

Critical step in the method is the formation of silicomolybdate which involves a rapid adjustment of the acidity of the sample in the presence of molybdic acid. This is accomplished by adding the sample extract to a mixture of molybdic acid and hydrochloric acid (and not vice versa). After 10 to 15 minutes, the reaction is assumed to be essentially complete. Once the silicomolybdate complex has formed, it can be either measured directly or changed to molybdenum blue and measured at ca. 800 nm. The silicomolybdate complex absorbs at 320/330 nm, but molybdic acid also absorbs strongly in this region.[1] This overlap makes the determination imprecise especially if a tungsten filament light source is used. Therefore, conversion to the blue compound is preferable.

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[☆] The method used is based on information detailed in the book "Fisheries Research Board of Canada, Bulletin No. 125, 2nd Ed. 1965: A Manual of Sea Water Analysis, by JDH Strickland and TR Parsons." Modifications, discussed here were made in the reducing agent and volumes of reagents and samples.

[1] VW Truesdale and CJ Smith: The Spectrophotometric Characteristics of Aqueous Solutions of $\alpha + \beta$ Molybdosilicic Acids. Analyst 100, 797-805, 1975.

Sensitivity for the blue compound is about 2 to 3 times higher than for the species read in the UV.

The reducing substance recommended in the paper is p-methylaminophenol. Since this compound was not available to us, we tried several other reducing compounds generally used for molybdate blue methods. In our trials, 4 compounds tested gave essentially the same results:

| | Absorbance at 810 nm with 1 ppm $SiO_2$ |
|---|---|
| p-aminophenol (most similar to the substance recommended) | 0.58 |
| ascorbic acid | 0.54 |
| 1, 2, 4 aminonapthol sulfonic acid | 0.54 |
| o-phenylenediamine | 0.56 |
| hydrazine | 0.43 |

In all cases except with hydrazine, sodium bisulfite was added as a preservative. Hydrazine was eliminated because of the slowness of the reaction. In most methods using hydrazine, this substance is heated to hasten reaction. All the organic substances except ascorbic acid were eliminated because of their yellow color, either before or after the reaction. A stock solution containing ascorbic acid and bisulfite in equal amounts has been found to remain stable for about one month. This same reducing substance was also suggested by Murphy and Riley[2] for the analysis of phosphate for reduction of phosphomolybdic acid to the corresponding Mo-blue. Other modifications to the original method involved proportionate reductions of volumes to scale the method to the samples analyzed.

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[2] Murphy and JP Riley: A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta, 27(1962), 31-36.

## Method for the Determination of Reactive Silicate in Small Samples of Aqueous Extracts from Atmospheric Particulate Matter

Reagent A: 80 ml of 2% ammonium molybdate solution

9 ml of 6 M hydrochloric acid

Make up to 100 ml. The solution is usable indefinitely unless a precipitate is seen.

Reagent B: In a 100 ml stoppered cylinder mix:

55 ml of 5 N $H_2SO_4$ (70 ml conc. $H_2SO_4$ to 500 ml with water)

15 ml of saturated oxalic acid solution (approx. 10%)

25 ml of 1% ascorbic acid containing 1% of sodium bisulfite.

Make up to 100 ml. Discard after 24 hours.

Procedure: In 10 ml Erlenmeyer flasks, place 1 ml of reagent A and add 5 ml of sample solution. Let react for 15 ± 5 min.

Add 4 ml of reagent B and let react for one hour ± 15 min.

Measure at 810 nm against a blank made with distilled water.

Compare with a calibration curve made with standards containing a maximum of 2 ppm $SiO_2$.

Standard: A 100 ppm $SiO_2$ solution is made by diluting 4.67 ml of a 1000 μg/ml Si standard (commercially available).

Range: With a 20 mm (or 25 mm) cell, the range is 0.2 to 2 μg/ml $SiO_2$.

With a 10 mm cell, the range is 0.5 to 4 μg/ml $SiO_2$.

With a 1 mm cell (10 mm cell + 9 mm spacer), the range can be extended to 40 μg/ml $SiO_2$.

Precision: The precision is better than 5% at all levels, when standards are run concurrently with the samples.

Working Curve: Figures A-1 and A-2 show the working curves used for silicate prepared from standards run before and after the samples.

Where only one point is visible, the two determinations were indistinguishable.

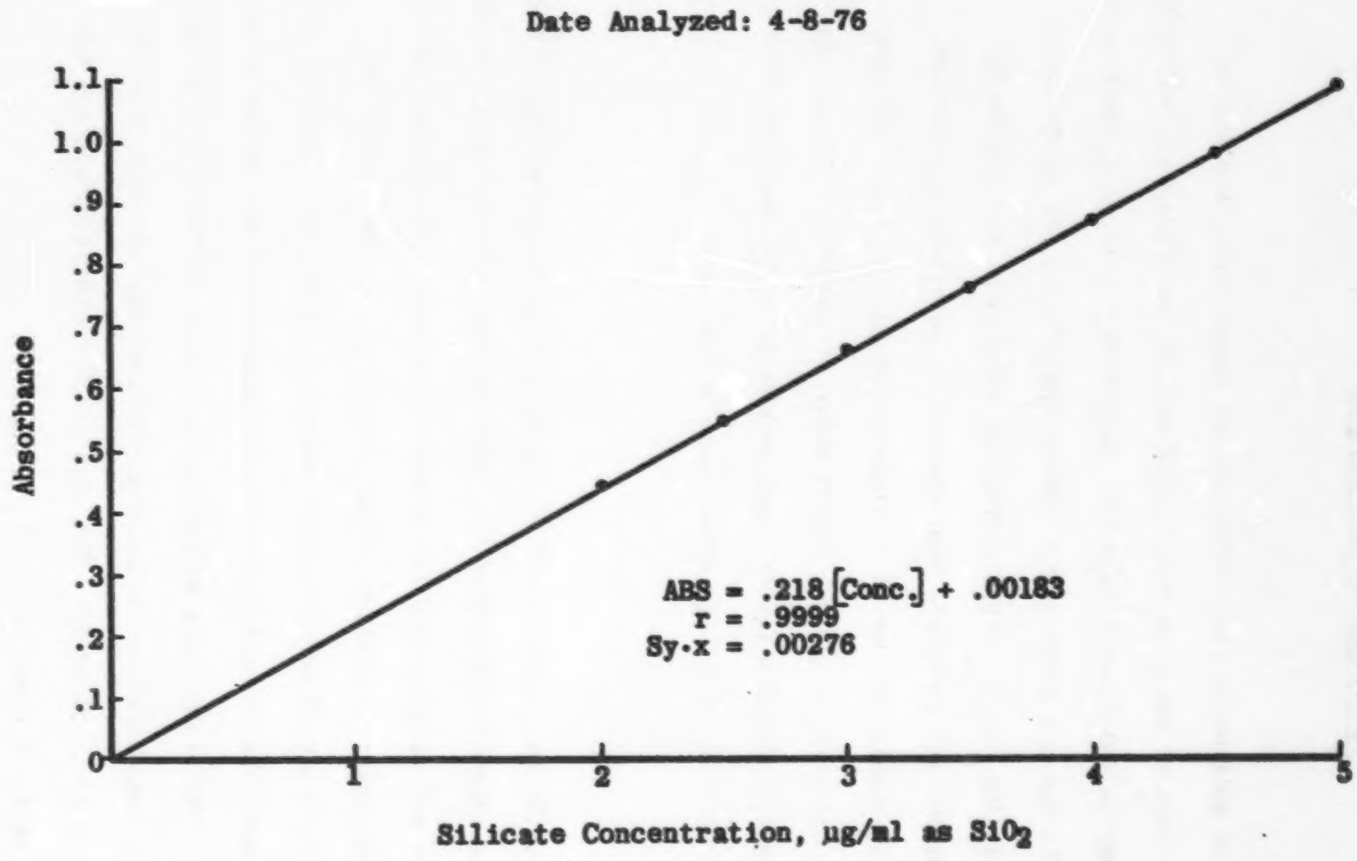

Figure F-1. $SiO_2$ determinations on quartz filters (date analyzed: April 8, 1976).

## Determination of Phosphate

### Introduction

The chemistry of molybdenum blue formation was exhaustively studied in the past three decades and as a result many methods for phosphate, silicate, arsenate, germanium and other metals were described. Generally, these methods are not specific and are cumbersome. Higher specificity can be obtained, however by employing low pH, organic reducing substances and complexing agents. The method for phosphate was improved by selecting appropriate conditions which enable the use of a single solution (1, 2) for the analysis. The procedure used here is a minor modification of the method in references 1 and 2. Changes involved a proportional reduction of the amounts of reagent which was necessary to handle the small samples available.

### Interferences

In this method, the only interferent of any significance is arsenate, which is 0.4 times as sensitive as phosphate. This element is only rarely occurring in concentrations affecting the phosphate results (the natural ratio is < 1:20). The color is measured either at 710 or 882 nm. About 20% higher sensitivity can be achieved when measuring at 882 nm. However, this wavelength is near the cut-off limit of most instruments and causes large instabilities. The second peak at 710 nm was chosen for use with our instrumentation. The concentration of the complexing metal, antimony, must be below 8 μg/ml to avoid clouding. The blue color contains phosphorus and antimony in a ratio of about unity.

## Reagents

Mix 32 ml of 5 N $H_2SO_4$ (made by diluting 70 ml conc. acid to 500 ml)

20 ml of 2% molybdate

35 ml of 1% ascorbic acid solution containing 1% Na bisulfite

3 ml of 1 mg/ml solution of Sb (0.274 g of K Sb tartrate to 100 ml)

Fill the mixture to 100 ml with distilled water and discard after 24 hours.

## Procedure

To three ml of sample solution add one ml of the reagent mixture. When using a 25 mm cell, these volumes must be doubled. Measure at 710 nm after 10 to 15 min.

## Range

A range of 0.3 to 4 ppm can be covered with a 25 mm cell. With shorter pathlengths, e.g. 10 mm, up to 80 ppm can be measured directly. Higher concentrations need aliquoting and dilution of samples.

## Standards

The 1000 ppm $PO_4^{\equiv}$ standard is made by dissolving 0.286 g $KH_2PO_4$ in 200 ml of distilled water. Dilute 1 ml to 100 ml with water for the working standard of 10 ppm. With a repetitive pipet make dilutions covering the desired range.

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1. J. Murphy and J. P. Riley: A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27, 31-36, 1962.

2. S. J. Eisenreich, R. T. Bannerman, D. E. Armstrong: A simplified phosphorus analysis technique. Environmental Letters 9(1), 43-53, 1975.

**Working Curve**

Figure B-1 illustrates the working curve used as prepared from standards run before and after the samples. Where only a single point is shown the two determinations are indistinguishable.

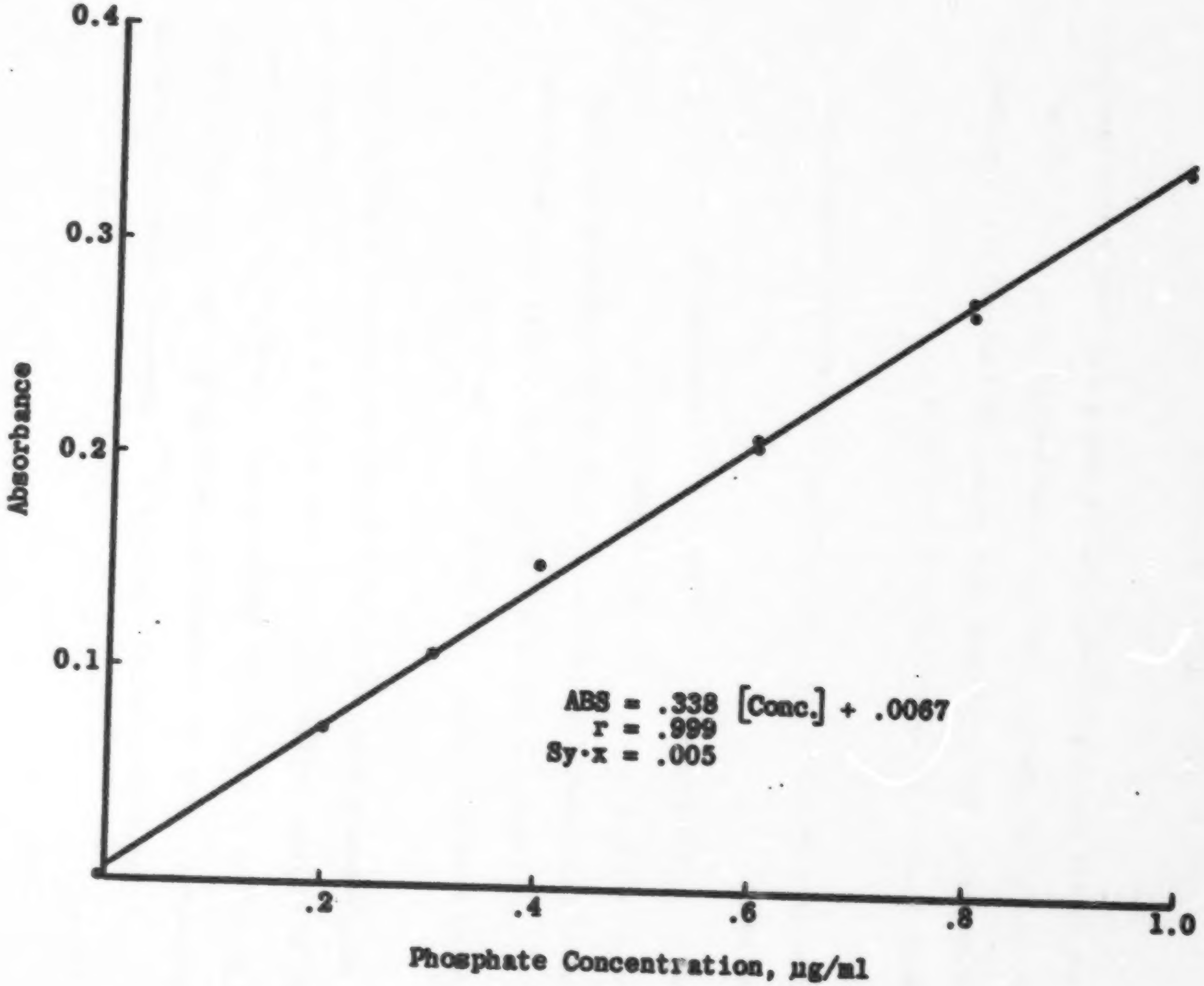

Figure G-1. Calibration curves for phosphate determination on selected quartz and glass total filters (May 14, 1976 calibration).

## Appendix H

## DETERMINATION OF SULFITE

Three on-inch filter discs, previously removed from glass total filter samples, were placed into 100 ml plastic screw cap vials containing 10 ml of 0.04 M tetrachloromercurate. The containers were capped and immersed into a minimal depth of water inside a sonicator bath for one minute.

After removal from the bath, the vials were uncovered and the following reagents were added:[*]

1 ml of 0.6% sulfamic acid. After 10 min. stabilization,
2 ml of a 1:200 dilution of 40% formaldehyde,
5 ml of pararosaniline solution (20 ml purified 0.2% pararosaniline
    diluted with 200 ml 3 M $H_3PO_4$ and 30 ml distilled water) and
2 ml of distilled water. The total volume was 20 ml.

After 20 min. reaction time, each filter sample was filtered by gravity through a 7 cm No. 40 Whatman filter into a dry test tube 16 x 200. The absorbance was measured at 580 nm in a 5 cm cell against water. A calibration line was measured concurrently. This was prepared by measuring aliquots of a precalibrated 10 $\mu$g/ml $So_2$ solution in tetrachloromercurate. Figure H-1 shows the resulting working curve.

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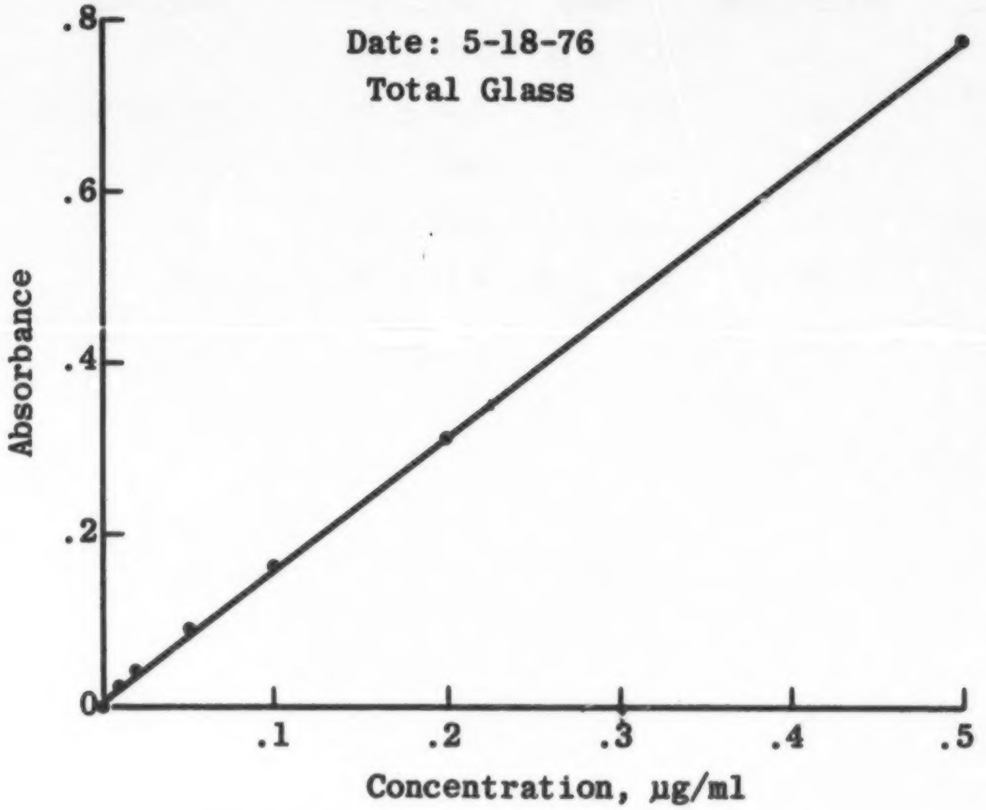
[*] Adapted with the modifications indicated for maximum sensitivity from Method 42401-01-69T, Intersociety Committee: Methods of Air Sampling and Analysis, American Public Health Association, 1972, Washington, D.C., pp 447-455.

## SULFITE CALIBRATION CURVE



$$ABS = .007 + 1.53 \; [Conc]$$
$$Sy \cdot x = .0021$$

Figure H-1

## Table H-1

## INTERLAB COMPARISON OF SULFITE DETERMINATIONS USING SMELTER DUST SAMPLES

| | | Sulfite, weight % | | |
|---|---|---|---|---|
| | | BYU | | AIHL |
| **Sample** | **Smelter Type** | **March** | **Oct. 1976** | **Sept. 1976** |
| 1 | Cu | 0.69 ± .1 | 1.03 ± .04 | 0 |
| 2 | Pb | none | 2.16 ± .62 | not determined |
| 3 | Pb | none | none | 0.021 |
| 4 | Cu | 1.54 ± .1 | 1.17 ± .1 | 0.002 |
| 5 | Pb | 0.85 ± .11 | 0.77 ± .09 | 0.85 |

## Appendix I

# X-Ray Fluorescence Analysis of St. Louis Aerosol Collected on Fluoropore Filters

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An X-ray fluorescence spectrometer was used for elemental analysis of the aerosol particles that were collected on Fluoropore filters using dichotomous samplers that were operated in St. Louis. The spectrometer was equipped with a secondary fluorescence-type excitation source and a Si(Li) type energy dispersive detector.[1,2] Elements with atomic numbers between 13 and 20 were analyzed using the nearly monoenergetic X-rays from a titanium fluorescer; elements with atomic numbers between 22 and 38 and Pb were analyzed using a molybdenum fluorescer.

The X-ray spectra for each sample were analyzed using a sequential stripping technique.[1,2] For this technique, a library of single element spectra corresponding to thin standards for all elements to be analyzed was stored in the memory of a minicomputer, which was used for the analysis. Also stored were spectra for a clean filter to represent the blank. Using the stripping technique, a linear combination of the stored single element spectra and blank was found which accurately fit the unknown spectrum. The amount of each component in this fit was assumed to be proportional to the concentration of each element in the sample.

The X-ray fluorescence spectrometer was calibrated using thin film standards obtained from Micromatter Co., Seattle, Washington. Each standard consisted of a 28 mm diameter deposit of 1 or 2 elements on a thin Mylar film. The deposits were prepared in a vacuum using vapor deposition. For each standard, the mass per unit area was determined from the measured weight gain of the substrate after the deposition and from the known area of the deposits. The sulfur standard consisted of sulfur and copper deposits of 28 $\mu g/cm^2$ and 91 $\mu g/cm^2$, respectively, on the Mylar film.

For analysis of sulfur, the K$\alpha$ line was used. For this line there is an interference from the M X-rays of lead. To correct for this interference, the true sulfur concentration was obtained from the lead concentration and from the uncorrected sulfur concentration using the relationship:

$$S(\text{true}) = S(\text{uncorr}) - K\ Pb$$

For the correction coefficient, the value K = 0.50 ± 0.05 was deduced by analyzing a thin film lead standard as if it were sulfur. With a 10% uncertainty in K, one can estimate the resulting uncertainty in the sulfur concentration due to the presence of lead. For samples collected at Regional Air Pollution Study (RAPS) Site 106 between August 18 and September 7, 1975, the mean lead and sulfur concentrations were 0.6 and 3.7 $\mu g/m^3$, respectively. Thus, the lead causes an uncertainty of 0.03 $\mu g/m^3$ for the sulfur, which amounts to only 0.8% of the mean sulfur concentration. At RAPS Site 124, the mean lead and sulfur concentrations were 0.13 and 3.0 $\mu g/m^3$, respectively, resulting in a 0.2% contribution to the uncertainty in the mean sulfur contribution.

For sulfur in the fine particle fraction, a correction was made for a theoretically predicted attenuation of the X-rays by the filter medium in which particles were collected.[3] This correction consisted of dividing the sulfur K X-ray yield by the factor 0.85.

The results from the X-ray fluorescence analysis of the samples from St. Louis were submitted in March 1976 to Dr. Bruce Appel of the Air and Industrial Hygiene Laboratory. More recently, it has been learned that the attenuation effect for the membrane filter is much smaller than the earlier theoretically predicted value, and that the appropriate attenuation factor should be 0.97 ± 0.03.[4] In addition, there is a need to make a small correction for the attenuation of the sulfur in the layer of particles collected on the filter. The net effect of the revised filter attenuation factor and the added layer attenuation factor will be to yield an overall factor that is close to the value of 0.85, which was used in the original analysis. A report describing these corrections in greater detail is now being prepared.

## References

1. Goulding, F.S. and J. M. Jaklevic. "X-Ray Fluorescence Spectrometer for Airborne Particulate Monitoring," EPA Report No. EPA-R2-73-182, April 1973.

2. Jaklevic, J.M., F.S. Goulding, B.V. Jarrett and J.D. Meng. "Applications of X-Ray Fluorescence Techniques to Measure Elemental Composition of Particles in the Atmosphere," in Analytical Methods Applied to Air Pollution Measurement, R.K. Stevens and W.F. Herget, Eds. (Ann Arbor, Michigan:Ann Arbor Science Publishers, 1974), pp. 123-146.

3. Dzubay, T.G. and R.O. Nelson. "Self Absorption Corrections for X-Ray Fluorescence Analysis of Aerosols, " in Advances in X-Ray Analysis, Vol 18, (New York: Plenum Publishing Corp., 1975), pp. 619-631.

4. Loo, B.W., R.C. Gatti, B.Y.H. Liu, C.S. Kim, and T.G. Dzubay. "Absorption Corrections for Submicron Sulfur Collected in Filters, " in X-Ray Fluorescence Methods for Environmental Samples. (Ann Arbor, Michigan: Ann Arbor Science, 1977).